BULLETIN OF THE ACADEMY OF SCIENCES OF THE U.S.S.R.

DIVISION OF CHEMICAL SCIENCES

1954

Number 4

July-August

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35903

IN ENGLISH TRANSLATION

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CONSULTANTS BUREAU
152 West 42nd Street
New York 36, N.Y.

Printed in the United States

Annual subscription $80.00
Single issue 20.00

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BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

DIVISION OF CHEMICAL SCIENCE

1954, [redacted]

[redacted]

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IN ENGLISH TRANSLATION

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CONSULTANTS BUREAU

152 West 42nd Street
New York 36, N. Y.

Printed in the United States

Annual subscription $80.00
Single issue 20.00

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Bulletin of the Academy of Sciences of the U.S.S.R., Division of Chemical Science
in English Translation

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DIVISION OF CHEMICAL SCIENCES

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January-February

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU
152 West 42nd St., New York 18, N.Y.

—An agency for the interpretation of international knowledge—

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CONSULTANTS BUREAU
152 West 42nd Street
New York 18, N. Y.

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in English Translation

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Number 2

March-April

IN ENGLISH TRANSLATION

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152 West 42 nd St., New York 18, N.Y.

—An agency for the interpretation of international knowledge—

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152 West 42nd Street
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152 West 42nd St., New York 18, N.Y.

—An agency for the interpretation of international knowledge—

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CONSULTANTS BUREAU
152 West 42nd Street
New York 18, N. Y.

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CONSULTANTS BUREAU
152 West 42nd St., New York 18, N.Y.

—An agency for the interpretation of international knowledge—

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Number 5

September - October

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CONSULTANTS BUREAU

259 WEST 14TH ST., NEW YORK 11, N. Y.

—An agency for the interpretation of international knowledge—

Bulletin of the Academy of Sciences of the U.S.S.R., Division of Chemical Sciences

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259 West 14th St., New York 11, N. Y.

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OBITUARY

ACADEMICIAN VLADIMIR MIKHAILOVICH RODIONOV

The death occurred on February 7, 1954, of Academician Vladimir Mikhailovich Rodionov, the eminent chemist, great technologist, and teacher, one of the founders of our synthetic dye industry and of the industry concerned with the preparation of alkaloids and pharmaceuticals.

V. M. Rodionov was born in Moscow on October 16 (28, New Style), 1878; he was educated in Moscow, graduating from the Moscow Technical High School.

His scientific activities have been characterized by the profundity of the investigations that he and his numerous students have carried out and by the wideness and variety of his scientific interests. He has published more than 150 scientific papers and has received more than 15 Author's Certificates for inventions; he has translated and edited about twenty important books and monographs on various branches of chemistry. He has discovered and developed new methods for the alkylation of organic compounds that are widely applied in the pharmaceutics and dye industries, and he proposed an original method for the preparation of diazophenolsulfonic acids, which are of great importance in the preparation of high-quality dyes. He has discovered also, methods, remarkable for their simplicity, for the synthesis of β-amino acids, which are of very great importance in biology. Of no less importance are the methods developed by Rodionov for the conversion of β-amino acids and their derivatives into various types of heterocyclic compounds, which are widely used for the synthesis of medicinals, vitamins, and antibiotics.

In the course of his long career as a teacher, Rodionov trained hundreds of talented technologists and investigators, including many who are now occupying responsible posts in industry, in the higher teaching establishments, and in the research institutes; some of his students have already established their own schools of investigation and have opened up new fields of work. More than thirty of his students are doctors of science, and more than seventy are candidates of science.

In addition to his scientific and teaching activities, Rodionov did much organizational work: he occupied a number of responsible positions in industry, and in the later years of his life he was president of the Technical Council of the Ministry of Chemical Industry.

V. M. Rodionov was a very significant figure in Soviet chemical circles. For many years he occupied responsible positions in the D. I. Mendeleev All-Union Chemical Society, and in his later years he was president of this society.

In 1939 he was elected a corresponding member of the USSR Academy of Sciences, and in 1943 he became an academician.

The Soviet government greatly appreciated Rodionov's services to his Fatherland, and he was awarded three Stalin prizes, the Order of Lenin, two Orders of the Red Banner of Labor, and a medal "For Valiant Work in the Great Patriotic War, 1941-1945".

In the loss of V. M. Rodionov, Soviet science has suffered a great blow. Scientists, industrial workers, and students will long retain vivid memories of Vladimir Mikhailovich Rodionov, as a great scientist, fervent patriot, and remarkable man.

Presidium of the USSR Academy of Sciences; Division of Chemical Sciences of the USSR Academy of Sciences; Ministry of Culture of the USSR; Ministry of Chemical Industry of the USSR; Ministry of Health of the USSR; D. I. Mendeleev All-Union Chemical Society.

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REACTIONS OF PHENOL WITH PHOSPHORUS

S. I. Volfkovich, V. K. Kuskov, and K. F. Koroteeva

As is well known, white and red phosphorus react with water at high temperature and under pressure, and various compounds are produced according to the conditions under which the reaction is carried out. When water vapor reacts with heated phosphorus, phosphorous acid and phosphine are formed [1], and when phosphorus and water react under pressure, phosphoric acid and hydrogen are formed [2], together with smaller amounts of other products. With aqueous solutions of caustic alkali, white phosphorus gives mainly hypophosphites and phosphine, and the same reaction occurs with red phosphorus at 130-170° under pressure.

In 1906 Berthaud [3] showed that the action of methanol and of ethanol on phosphorus is analogous to that of water: in a sealed tube at 250° or higher, alkylphosphonic and alkylphosphonous acids, alkylphosphines, phosphonium salts, and inorganic phosphorus compounds are formed. In 1907 Senderens [4] found that in presence of red phosphorus intramolecular dehydration of ethanol occurs. We have repeated Berthaud's reaction of phosphorus with ethanol in an autoclave at 240-250° under 100 atm, and have obtained a mixture of phosphorus-containing products, including products of b.p. 110-220°, the structures of which have not been established. The gaseous reaction products included ethylene, formed evidently by Senderens' reaction. The total yield of phosphorus-containing products was very small. When the reaction temperature was raised, decomposition products were obtained in appreciable amounts. A comparison of results described in the literature with our observations suggests that first of all dehydration of the alcohol occurs. The water formed by this reaction then reacts with phosphorus, and the molecules, ions, or radicals formed react with the alcohol, yielding various organic and inorganic phosphorus compounds. It is thus considered that the formation of these phosphorus compounds is the result of secondary reactions.

In the present investigation, we have studied the reaction of phosphorus with phenol, i.e., with an alcohol that is unable to undergo intramolecular dehydration. It was found that phenol does not react with red phosphorus, even at 300° in an autoclave. When a mixture of phenol, phosphorus, and a small amount of water is heated in an autoclave, a reaction sets in already at 200°: the pressure begins to rise rapidly and, irrespective of temperature and ratio of reactants, it attains 40-150 atm. From the products of this reaction, apart from unchanged phenol and the usual reaction products obtained from phosphorus and water (phosphoric and phosphorous acids, hydrogen, and phosphine), we have isolated phenylphosphine, diphenylphosphine, triphenyl phosphate, and also a water-soluble phosphorus-containing compound, which was considered to be phenylphosphonic acid, although it was not found possible to isolate this substance in an analytically pure state.

When phosphorus reacts with a mixture of phenol and sodium or potassium phenoxide in absence of water, reaction proceeds at 270°, and the pressure attains 56 atm. The main reaction product is diphenyl ether, and only qualitative indications of the presence of phosphorus-containing compounds were obtained. Reaction between phenol and phenoxide evidently occurs (intermolecular dehydration of phenol in presence of phenoxide as catalyst). The formation of traces of phosphorus compounds is evidently due to the action of phosphorus on water formed in the intermolecular condensation. When water is added, the reaction occurs even at 150°, and from the reaction mixture, apart from inorganic phosphorus compounds and unchanged phenol, phenylphosphine, triphenyl phosphate, and phenylphosphonic acid (contaminated with phosphates) may be isolated. Thus, when phosphorus reacts with phenol and a phenoxide in presence of water, a dismutation reaction occurs, probably by a chain mechanism analogous to that found in the reaction of phosphorus with water and aqueous solutions of alkalis; but, instead of inorganic phosphorus acids and phosphine, their phenylated analogs are obtained. Instead of phosphoric acid, therefore, triphenyl phosphate should be obtained, instead of phosphine – phenylphosphine, and finally, instead of phosphorous acid (or phosphites, such as $HPO(ONa)_2$) phenylphosphonic acid or disodium phenylphosphonate might be expected to be formed. These organic substances were in fact obtained in our experiments.

In accordance with the above, the formation of the organophosphorus compounds may be described in terms

of classical structural theory by means of the following equations:

$$2P + 2H_2O + 6C_6H_5OH \longrightarrow 2(C_6H_5O)_3PO + 5H_2;$$

$$2P + 2H_2O + C_6H_5ONa \longrightarrow C_6H_5PH_2 + NaH_2PO_2;$$

$$2P + 2H_2O + C_6H_5ONa \longrightarrow PH_3 + C_6H_5PO(OH)(ONa);$$

$$2P + H_2O + 2C_6H_5ONa \longrightarrow C_6H_5PH_2 + C_6H_5PO(ONa)_2.$$

The process is, however, considerably more complicated, and these equations indicate only the result of the reaction, and not its mechanism. It may be noted that at above 250° red phosphorus was converted into black, whereas at below 250° partial transformation into white occurred.

EXPERIMENTAL

Reaction of Phenol with Phosphorus in Presence of Water

A carefully blended mixture of 23.5 g (0.25 mole) of phenol, 6.8 g (0.22 mole) of red phosphorus, and 4.5 ml (0.25 mole) of water was introduced into a vertical 50-ml autoclave, and was heated at 250-265° under a pressure of 110 atm for 4 hours 30 minutes. The autoclave was set aside for twelve hours to cool, and the pressure was then 20 atm. Analysis showed that the gaseous products contained 99.5% of hydrogen. The mixture was diluted with water, and unchanged red phosphorus was filtered off, washed with ether, and vacuum-dried (5 g). The aqueous filtrate and ether washings were heated in a bath to remove ether, and the residue was extracted three times with 50-ml portions of benzene. The benzene extract was dried with magnesium sulfate, the benzene was driven off, and the residue was vacuum-distilled at 3 mm. Fractions boiling at 87-96° and 170° were collected. The first fraction was 2.8 g (0.025 mole) of phenylphosphine, which was redistilled under atmospheric pressure (b.p. 160°).

Analysis (Marie's method)

Found %: P 27.63; 27.67

C_6H_7P. Calculated %: P 28.18

The second fraction was 1 g (0.062 mole) of diphenylphosphine, b.p. 272° at atmospheric pressure.

Found %: P 15.92; 15.84

$C_{12}H_{11}P$. Calculated %: P 16.6

Phenol was removed from the aqueous portion by steam distillation, and the residue was evaporated down. The solid residue was dried on a water bath and then in a vacuum desiccator over phosphoric oxide. The product was 4 g of a yellowish hygroscopic crystalline substance containing 16% P (Marie's method). Calculation for phenylphosphonic acid ($C_6H_7PO_3$) gives 19.8% P. The product contained carbon and hydrogen and gave the typical copper, iron, and barium salts of phenylphosphonic acid.

In another experiment in which half the amount of water was used (2.25 ml, i.e., 0.12 mole) (200°, 50 atm, 16 hours), an analogous treatment yielded diphenylphosphine and a mixture of phosphorous acids, as in the preceding experiment.

Reaction of Sodium Phenoxide with Phosphorus

a) In Presence of Water. A carefully blended mixture of 8.2 g (0.26 mole) of red phosphorus, 23.2 g (0.2 mole) of dry sodium phenoxide, and 3.6 g (0.2 mole) of water was introduced into the autoclave. The temperature was raised gradually to 250° over a period of four hours, when the pressure had attained 47 atm. This temperature was maintained for three hours, and the autoclave was allowed to cool over twelve hours, when the pressure became 30 atm; the gas present consisted of hydrogen and phosphine.

The gaseous products were released through a needle valve, and the mixture was extracted from the autoclave with 200 ml of hot water. The mixture was neutralized with hydrochloric acid, and unchanged phosphorus was filtered off under suction, washed with ether to remove organic substances, and dried. The phosphorus so obtained (4 g) was violet in color. The aqueous extract and ether washings were united and heated in a bath to remove ether. The oily layer that formed was extracted with benzene, and the extract was dried with magnesium sulfate and distilled. After removal of benzene and unchanged phenol, 0.7 g (0.0064 mole) of a colorless heavy oil having a characteristic phosphine odor came over under reduced pressure, b.p. 80-90° (3 mm); its boiling point at atmospheric pressure was 150-160°, which corresponds to phenylphosphine.

Phenol was steam-distilled from the aqueous layer, and the residue was evaporated until crystals appeared. The common salt was filtered off, and the residue was again evaporated until crystals appeared. The mixture was cooled, and the precipitate was filtered off and recrystallized from water, yielding 1 g of an organic substance that gave qualitative reactions for sodium phenylphosphonate: precipitates with copper sulfate (blue), ferric chloride (dark brown), and barium and calcium chlorides (white). When it was heated with zinc dust, there was a characteristic phosphine odor. Analysis for phosphorus, however, gave a value higher than that calculated;

Found %: P 17.05; 17.01

$C_6H_5PO_3Na_2$. Calculated %: P 15.2

The sodium phenylphosphonate obtained was apparently contaminated with sodium phosphate. The remaining filtrate was evaporated until crystallization occurred; cooling and filtration then yielded 1.4 g of disodium hydrogen phosphate.

When the amount of water taken was doubled (7.2 ml, i.e., 0.4 mole) (150° for 8 hours, 225° for 4 hours, 260° for 4 hours, and a maximum pressure of 60-90 atm), only traces of phosphines were obtained after a similar treatment, but distillation of the benzene extract yielded 1-2 g of triphenyl phosphate, b.p. 215° (4 mm) (colorless crystals, m.p. 48.5°). The literature gives m.p. 49-50°, b.p. 245° (11 mm).

Found %: P 9.26

$C_{18}H_{15}O_3P$. Calculated %: P 9.50

Hydrolysis of the product at the boil with 10% caustic soda solution for two hours gave phenol (positive reaction with bromine water and ferric chloride) and sodium phosphate (positive reaction with ammonium molybdate). In each of these experiments we obtained from the aqueous layer a phosphorus-containing organic substance, apparently impure phenylphosphonic acid, and about 5 g of a mixture of sodium phosphate and sodium phosphite.

b) In Absence of Water. A mixture of 13.5 g (0.09 mole) of sodium phenoxide, 17 g (0.18 mole) of phenol, and 3.96 g (0.12 mole) of red phosphorus was heated for two hours at 200° in an autoclave. The pressure attained 52 atm. The autoclave was heated further for one hour at 270°, and the pressure attained 56 atm. When the autoclave had cooled, the residual pressure was 30 atm. The gaseous products contained phosphine. The reaction mixture was treated as described above. Distillation of the benzene extract yielded 3 g of a substance of b.p. 160° (3 mm), and fractionation of this at atmospheric pressure yielded 2.3 g of a substance of b.p. 258°; qualitative tests indicated only carbon and hydrogen. The product corresponded in appearance, analysis, and boiling point to diphenyl ether.

Found %: C 83.8; H 6.35

$C_{12}H_{10}O$. Calculated %: C 84.4; H 5.9

The investigation has thus shown that it is possible to obtain aromatic organophosphorus compounds by the direct action of phenol or of a phenoxide on elementary phosphorus.

SUMMARY

1. When phenol, or a mixture of phenol and sodium phenoxide, is heated with red phosphorus under pressure and in presence of water, a mixture of phosphorus-containing organic compounds is obtained; it contains phenylphosphine, diphenylphosphine, and triphenyl phosphate.

2. When a mixture of phenol, sodium phenoxide, and red phosphorus is heated under pressure in absence of water, diphenyl ether and traces of organophosphorus compounds of unknown structure are obtained.

3. In absence of water, phenol does not react with red phosphorus, either at atmospheric pressure, or at elevated pressures.

4. A hypothesis is advanced concerning the nature of the reaction of phosphorus with phenol under the experimental conditions used.

Received June 28, 1953.

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COMPOUND OF HYDROGEN SULFIDE WITH PHENYLHYDRAZINE

B. A. Nikitin* and M. F. Pushlenkov

Compounds of inert gases with phenol and with toluene were first prepared by Nikitin [1] by the method of isomorphous coprecipitation. The compounds with phenol have the formula $A \cdot C_6H_5OH$, and those formed with toluene have the formula $A \cdot 2C_6H_5CH_3$, where A denotes an inert-gas atom. Later, a compound of radon and p-chlorophenol was obtained [2], and this had the formula $Rn \cdot 3ClC_6H_4OH$. These benzene derivatives form similar compounds with volatile hydrides, in particular, H_2S.

Terres and Vollmer [3] studied the melting point diagram of the phenol–hydrogen sulfide system, which indicated the presence of a molecular compound between hydrogen sulfide and phenol of the type $H_2S \cdot 2C_6H_5OH$. By means of a specially developed technique, we determined the melting point diagram of this system with greater accuracy [4], and we showed that the compound formed between phenol and H_2S has the formula $H_2S \cdot 3C_6H_5OH$. In investigations by Nikitin [5, 6, 7] it has been shown the most stable molecular compounds of the inert gases and their analogs, the volatile hydrides, are those formed with phenol.

We have now made a study of a benzene derivative, phenylhydrazine, with the object of preparing its compound with hydrogen sulfide. According to the literature [8], the compound of phenylhydrazine with hydrogen sulfide has the formula $H_2S \cdot C_6H_5NH \cdot NH_2$. However, the experimental procedure employed in this work [8] is open to some doubt, and so also, therefore, is the formula advanced for the compound. Although there was every indication that the compound was able to dissociate, the authors of this paper took no particular precautions and analyzed the compoud obtained by the usual chemical method, a procedure that quite often leads to erroneous conclusions in such cases.

EXPERIMENTAL

The formation of the compound of phenylhydrazine with hydrogen sulfide was studied by the thermal-analysis method, the procedure being that already employed for analogous systems [4]. Since the system contains a volatile component, it was first necessary to obtain the temperature-pressure diagram (t-p) in order to permit a correction for the H_2S remaining in the gas phase to be made (in the calculation of the molecular ratio of components), when plotting the melting point diagram. The phenylhydrazine used in these investigations melted at $19.1 \pm 0.1°$; the hydrogen sulfide melted at $-85.0 \pm 0.3°$.

A weighed sample of phenylhydrazine was introduced into a glass ampoule, 1.0-1.5 ml in volume, which was then sealed to a mercury-in-glass monometer reading up to 8 atm (the other limb of the manometer was closed). Air was pumped from the apparatus via a side tube, the ampoule was cooled with liquid air, and H_2S was admitted from a buret graduated accurate within 0.1 ml. The side tube was then sealed off, so that the apparatus was hermetically closed (a small electromagnetic stirrer was introduced into the ampoule before it was sealed off). In order to establish the equilibrium pressure in the ampoule, this was kept for a long time at a definite temperature in a cryostat or thermostat that permitted direct observation to be made. During this time the liquid was vigorously and continuously stirred with the electromagnetic stirrer. When the equilibrium pressure was established in the vessel, it was recorded as the value for that particular temperature.**

The curve APH shows the variation of pressure with temperature for the equilibrium of three phases: solid phenlhydrazine, the liquid phase, and gaseous H_2S. The curve PMC corresponds to the case in which gaseous hydrogen sulfide, melt, and solid compound are in equilibrium. The curve DBP corresponds to the variation of the dissociation pressure of the solid compound (dissociating into solid phenylhydrazine and gaseous hydrogen sulfide); the section BP was determined experimentally, and the section DB was calculated (see below).

We give for comparison the curve EC, which shows the variation of the vapor pressure of H_2S over the liquefied gas with temperature. The section PH on the diagram corresponds to a metastable condition of three phases: solid phenylhydrazine, a solution of phenylhydrazine saturated with hydrogen sulfide, and gaseous H_2S. The intersection P (1.5°) of the curves APH and PMC corresponds to the upper eutectic point, at which four phases are in equilibrium:

* Deceased

** The results are listed in Table 1 and presented graphically in Fig. 1. The first 22 readings given in Table 1 correspond to the curve APH in Fig. 1, and the remaining readings correspond to PMC.

TABLE 1

Temp (°C)	Pressure (atm)	Temp. (°C)	Pressure (atm)	Temp. (°C)	Pressure (atm)	Temp. (°C)	Pressure (atm)
19.0	0.00	0.0	3.91	−14.0	5.48	−76.0	0.36
18.0	0.27	−1.0	3.96	−20.0	4.93	−80.0	0.27
		−3.0	4.08	−24.0	4.45	−81.0	0.24
17.0	0.71	−5.0	4.16	−26.0	4.12	−84.0	0.22
16.0	1.27			−28.0	3.88	−85.0	0.21
15.0	1.67	1.2	4.18	−30.0	3.62	−86.0	0.19
14.0	1.87	0.8	4.45	−32.0	3.36	−87.0	0.18
13.0	2.07	0.5	5.02	−34.0	3.12	−88.0	0.18
12.0	2.20	0.2	5.20	−36.0	2.70	−89.0	0.17
11.0	2.38	−1.0	5.70	−40.0	2.45	−90.0	0.16
10.0	2.78	−2.0	5.90	−44.0	2.12		
9.0	2.92	−3.0	5.92	−46.0	1.93		
8.0	3.05	−4.0	5.96	−50.0	1.60		
7.0	3.20	−5.0	6.00	−54.0	1.32		
6.0	3.30	−6.0	6.00	−58.0	1.09		
5.0	3.49	−7.0	5.98	−62.0	0.82		
4.0	3.60	−9.0	5.91	−66.0	0.65		
3.0	3.78	−11.0	5.80	−70.0	0.51		
2.0	3.86	−14.0	5.62	−74.0	0.40		

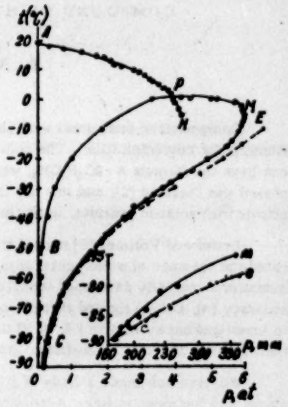

Fig. 1

solid phenylhydrazine, solid compound, melt, and gaseous H_2S. The point C on the t—p diagram corresponds to the lower eutectic point of the compound and solid H_2S (−87.5°). Thus, in the area DBPA we have solid phenylhydrazine and gaseous H_2S, and the area DBPMC corresponds to the simultaneous existence of solid compound and gaseous H_2S. It can be seen from this diagram that a compound is formed in this system having a maximum melting point of 1.5° at a maximum pressure of 6.0 atm.

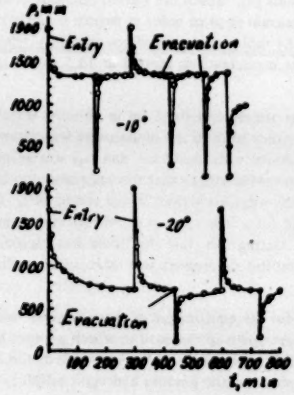

Fig. 2

In order to determine the dissociation pressure of the compound, a 6-8-g sample of phenylhydrazine was taken, cooled to −15.0°, ground to a powder without access of atmospheric moisture, and introduced into a 6-8-ml ampoule. The ampoule was immersed in liquid air and sealed to a graduated manometer. The vessel was then immersed in a cryostat, and hydrogen sulfide was passed into it. The vessel was held for periods at various temperatures until the first crystals of the compound appeared, after which the reaction went fairly quickly. When each fresh portion of hydrogen sulfide was admitted, the pressure rose, and then fell to a value that was definite and constant at the given temperature. It was found that, by continual admittance of fresh portions of hydrogen sulfide, the whole of the phenylhydrazine could be caused to react. When a sufficient amount of the compound had been formed and equilibrium pressure had been established, H_2S could be removed from the gas phase. The pressure in the vessel would then fall, and then, owing to the dissociation of the compound, it would rise to the equilibrium value, and this process could be repeated until the whole of the compound had been decomposed into phenylhydrazine and hydrogen sulfide. By way of example the course of the attainment of the equilibrium dissociation pressure following successive admittances and removals of H_2S is shown in Fig. 2 for experiments at −10° and −20°. In this way the dissociation pressure of the compound was determined at various temperatures; the results are given in Table 2.

On the basis of the results given in Table 2 (for temperatures from +1.4° to −50°), an empirical equation (Equation 1) was derived for the dependence of dissociation pressure on temperature; it permits the calculation of the

of the dissociation pressure accurate within ±3%.

$$\log p = \frac{A}{T} + B, \qquad (1)$$

in which p is the pressure (mm Hg), T is the absolute temperature, and A and B are constants, which are determined graphically.

TABLE 2

Dissociation pressure (mm Hg)	Calculated										
	2880	2510	1347	719	367	179	83	32	12	4	2
Temp. (°C)	1.4	0.0	−10	−20	−30	−40	−50	−60	−70	−80	−90

The experimental determination of the dissociation pressure of the compound at below −60° was practically impossible, because equilibrium is established very slowly at these temperatures. The dissociation pressure was, therefore, calculated from Equation 1. The dissociation pressure results are shown on the t—p diagram by the curve PBD, the section BD of which was calculated by Equation 1. Having determined the dissociation pressure of the compound at various temperatures below the eutectic point, it was possible to calculate the formation temperature of the compound by Clapeyron's equation, which may be transformed into the form

$$\log p = \frac{Q}{2.303R} \cdot \frac{1}{T} + \text{const}, \qquad (2)$$

in which p is the dissociation pressure (mm Hg), Q is the heat of formation of the compound (cal/mole), T is the absolute temperature, and R is the gas constant.

We may find Q, therefore, by a comparison of Equations 1 and 2 (Q = 2.303RA), or graphically. The value of Q found in this way was 8500 cal/mole.

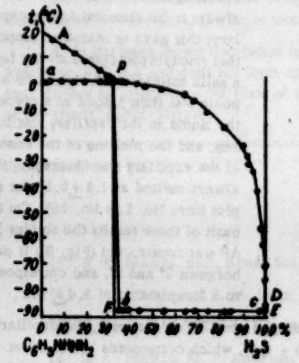

Fig. 3

Much supercooling occurs in the phenylhydrazine—H_2S system, and the determination of the melting point diagram by the temperature-arrest method is, therefore, not possible. The liquidus line was determined visually by observing the temperature at which the last crystal disappeared when the liquid was being stirred continuously. The solidus line was determined at temperatures close to the eutectic points by the centrifugation method developed previously [9].

The reaction vessel was a glass ampoule, volume 1.0-1.5 ml and having a ground joint at one end. A weighed amount of phenylhydrazine was introduced into the ampoule, and the electromagnetic stirrer was dropped in. The air was pumped out of the ampoule, and the required amount of H_2S was admitted by means of a tap attached at the ground joint. The H_2S was condensed, and the ampoule was sealed off while at the temperature of liquid air. The ampoule was then held at various temperatures in order to make sure that no compound was present. In the determination of the liquidus curve, the contents of the ampoule were heated until they melted, and were then frozen with liquid air; the ampoule was then immersed in a thermostat or cryostat (depending on the melting point). The ampoule was warmed slowly while its contents were stirred vigorously, and the temperature at which the last crystal disappeared was noted. The results of the experiments on the determination of the liquidus line are given in Table 3, and the melting point diagram in Fig. 3 was constructed from these results.

The liquidus line APCD consists of three curves: AP corresponds to the crystallization of pure phenylhydrazine, PC to the crystallization of the compound, and CD to the crystallization of H_2S. Two eutectic points were found on the liquidus curve: 1.4 ± 0.1° (33.3 mole % of H_2S) and −87.5 ± 0.3° (99.8 mole % H_2S).

The solidus line was determined on the sample used for the liquidus determination, or a new, similar sample was prepared.

TABLE 3

Ampoule No.	Mole-% of H_2S	Temp. of completion of melting (°C)	Ampoule No.	Mole-% of H_2S	Temp. of completion of melting (°C)
1	0.00	19.2			
2	4.80	17.4	2	3.50	+1.4
3	9.55	15.0	3	9.00	+1.4
4	14.56	12.7	4	14.20	+1.4
5	19.46	9.2	5	19.20	+1.4
6	26.20	5.8	6	26.10	+1.4
7	29.70	3.8	7	29.70	+1.4
8	31.23	3.0	9	31.20	+1.4
9	32.17	2.4	9	32.15	+1.4
10	32.50	2.0	10	32.70	+1.4
11	33.91	1.4	11	34.40	−87.5
12	34.76	1.2	12	35.10	−87.5
13	36.27	1.0	13	36.50	−87.5
14	38.44	0.8	14	39.10	−87.5
15	43.48	+0.2	15	44.00	−87.5
16	47.13	−0.2	16	54.80	−87.5
17	54.21	−2.0	17	64.40	−87.5
18	63.26	−6.2	18	68.30	−87.5
19	64.02	−7.6	19	74.00	−87.5
20	73.85	−10.5	20	81.50	−87.5
21	81.29	−16.8	21	94.40	−87.5
22	90.20	−24.0	22	96.10	−87.5
23	91.72	−28.0	23	99.00	−87.5
24	92.56	−31.0			
25	94.37	−33.5			
26	96.06	−41.0			
27	97.68	−54.5			
28	98.97	−62.0			
29	99.56	−70.5			
30	99.64	−75.5			
31	99.75	−85.5			
32	99.78	−87.5			
33	99.88	−86.0			
34	100.00	−85.0			

The contents of the ampoule were frozen, and were then placed in melting ice or chloroform, where the ampoule remained for 20 minutes It was then placed capillary downward in a centrifuge bucket filled with melting ice or chloroform (m.p. −63°), and was centrifuged for three minutes at 3000 r.p.m. The ampoule was then removed and examined for the presence or absence of liquid phase in the capillary. When liquid phase was present, the ampoule was immersed in the cryostat capillary downward; the liquid phase was then frozen and its melting point was determined. For systems poorer in hydrogen sulfide than the compound, liquid phase was absent after centrifugation at 0°; for systems richer in hydrogen sulfide, liquid phase was always to be observed. When liquid phase was absent, the ampoule was immersed in melting dimethylaniline, m.p. 2.0 ± 0.1°, and centrifuged while so immersed. After centrifugation, liquid phase was always to be observed in the capillary; this gave us reason to suppose that phenylhydrazine does not form a solid solution with H_2S. The ampoule was then placed in a cryostat, the liquid in the capillary was frozen, and the melting of the contents of the capillary was observed; they always melted at 1.4 ± 0.1° (for samples from No. 1 to No. 10). On the basis of these results the solidus line AP was constructed (Fig. 3); it passes between 0° and 2°, and corresponds to a temperature of 1.4 ± 0.1°.

In the experiments with ampoules No. 11 to No. 23, which were centrifuged at −63° (chloroform), the capillary always contained liquid phase, and this, when frozen, melted again at −87.5 ± 0.3°, which corresponds to the lower eutectic point on the melting point diagram. On the basis of these results, the solidus line bc, corresponding to this temperature, was constructed on the melting point diagram.

After the experiment the ampoule was opened and its volume was determined. The volumes of the stirrer and of the liquid or solid phase were subtracted from this volume. The amount of hydrogen sulfide remaining in the gas phase was calculated from the t–p diagram, and this was subtracted from the amount taken for the experiment. Since the maximum pressure in the system did not exceed 6.0 atm, the correction for the volume of the gas phase was 2.0-2.5% with respect to the amount taken for the experiment. On the solidus line at 0° no liquid phase was to be observed up to 32.7 mole-% H_2S, and for 34.4 mole-% of H_2S and higher, liquid phase was absent at temperatures below −87.5°.

Although there is no clearly defined maximum on the liquid curve, the presence of a sharp drop in the solidus line from 1.4° to −87.5° over a range of 1.7 mole-% of H_2S proves that in the system

$$C_6H_5NH \cdot NH_2 - H_2S$$

a compound is formed between phenylhydrazine and H_2S. The line PbF, along which the system consists of one component (the compound), may be produced through the point P to the axis of abscissas to the point corresponding within experimental error to 33.3 mole-% of H_2S. The formula of the compound is therefore $H_2S \cdot 2C_6H_5NH \cdot NH_2$.

Knowing that H_2S is an analog of the inert gases, it might be expected that radon would be isomorphously coprecipitated with it, owing to the formation of an analogous compound with phenylhydrazine. In order to put this to the test, we carried out a series of experiments over a wide temperature range ($-10°$ to $-70°$), in which we studied the action of a gaseous mixture of hydrogen sulfide and radon on solid phenylhydrazine. It was established that radon does not enter into the compound, even in experiments in which 90% of the hydrogen sulfide taken reacts with phenylhydrazine with formation of $H_2S \cdot 2C_6H_5NH \cdot NH_2$.

In this case, therefore, H_2S cannot be regarded as an analog of the inert gases. The compound obtained, $H_2S \cdot 2C_6H_5NH \cdot NH_2$, cannot, therefore, be classed as a molecular compound formed by Van der Waals forces; it is more probable that it is to be classed as an ammonium compound of the type $(C_6H_5NH \cdot NH_3)_2S$, in which phenylhydrazine plays the part of ammonia.

SUMMARY

1. The melting point diagram of the system $C_6H_5NH \cdot NH_2$—H_2S has been determined by the method of thermal analysis. No clearly defined maximum has been found in the system. The curve for the composition passes through a transition point at which the maximum and eutectic point coincide and correspond to a composition of 33.3 mole-% of H_2S at $1.4 \pm 0.1°$, which is that required by the compound $(C_6H_5NH \cdot NH_2)_2S$.

2. The t—p diagram has been determined in the presence of three phases (solid, liquid, and gas), so that, when determining the melting point diagram, a correction could be introduced for the amount of volatile component remaining in the gas phase.

3. The dissociation pressure of the solid compound (dissociating into solid phenylhydrazine and gaseous H_2S) has been determined. At 0° the dissociation pressure is 3.3 atm, thus indicating the low stability of this compound.

The heat of formation of the compound from solid phenylhydrazine and gaseous H_2S has been determined from dissociation pressure data, the value obtained being 8500 cal/mole.

4. It has been shown that radon is not isomorphously coprecipitated with the compound formed by phenylhydrazine with H_2S and does not form an analogous compound with phenylhydrazine. The compound obtained, therefore, cannot be assigned to the class of molecular compounds, but must be regarded as an ammonium compound, i.e., of the type $(C_6H_5NH \cdot NH_2)_2S$.

Received March 20, 1953

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CONDITIONS FOR THE SEPARATION AND GRAVIMETRIC DETERMINATION OF SILICIC ACID

COMMUNICATION 2. POLYMERIZATION OF SILICIC ACID

E. N. Egorova

Investigation of the procedure used in the dehydration method of separating silicic acid from solution has shown that separation of the acid by two dehydration treatments is not complete, even when optimum conditions are observed. The systematic discrepancies observed in parallel tests in the SiO_2 values found led to the supposition that the amount of silicic acid separated from solution depends not only on the dehydration conditions and the further treatment given to the precipitate, but also on the polymerization process to which the silicic acid has been subjected, prior to this treatment. If in the course of the evaporation of the acid solutions polymerization of silicic acid does not go to completion, then some of the silicic acid will remain in the form of simple nonpolymerized particles in the dry residue. During the further treatment of the dry residue and the dissolution of salts, this portion of nonpolymerized, or only slightly polymerized, silicic acid will again pass into solution.

The question of the polymerization of silicic acid arises also in connection with the completeness of its separation with the aid of coagulants in rapid methods of estimation. As would be expected, the completeness of the separation of silicic acid with the aid of coagulants depends on the extent to which the silicic acid passes into the colloidal state, i.e., on the extent to which polymerization occurs. This idea is not new: already in 1940 Weiss and Sieger [1] concluded that it is essential to give a prior treatment of the silicic acid in solution with concentrated solutions of mineral acids, in order to ensure that its conversion into the colloidal condition is as complete as possible before the coagulant is introduced.

The questions of the extent to which the polymerization of silicic acid in aqueous solution proceeds and of its reversibility have remained obscure. The published work on the polymerization of silicic acid has been carried out under conditions that do not correspond to those employed in its analytical determination, and this work is, therefore, not altogether applicable to the elucidation of the behavior of silicic acid in the course of analysis. Myilius and Groschuff [2] have investigated the polymerization of silicic acid in neutral solutions.

These authors obtained solutions of silicic acid by neutralizing solutions of sodium disilicate ($Na_2Si_2O_5$) with hydrochloric acid. The authors point out that, when the disilicate solution is rapidly neutralized with an equal volume of hydrochloric acid at 0°, the resulting neutral solution of silicic acid does not react with albumen; after long heating or standing, however, addition of albumen produces a turbidity.

When the disilicate solution is neutralized gradually, with heating after each addition of a fresh portion of hydrochloric acid, the resulting neutral solution forms a precipitate with albumen. Since silicic acid solutions that do not react with albumen acquire the ability to react after standing for a few days, these authors concluded that in neutral solution silicic acid is more stable in the form of polymers. On the basis of their investigations the authors divided silicic acids differing in degree of polymerization into two conventional groups: α- and β-silicic acids.

The concept of α-silicic acid introduced by these authors is a conventional one having only relative significance, for it relates to silicic acids of varying degree of polymerization, but having molecules that have not attained a sufficiently large size to be precipitable by albumen. The authors use the term β-silicic acid for the more highly polymerized forms, which are precipitated by albumen. The authors gave no indication of the limit of polymerization (i.e., degree of complexity) of α-silicic acid, but merely pointed out that the solutions that they obtained of the least complex silicic acids underwent polymerization in the course of time, and the rate of this reaction was increased by heating the solutions. Flemming [3] showed that the presence of small amounts of acids or alkalis in a silicic acid solution accelerates transition from true to colloidal solution.

Willstätter, Kraut, and Lobinger [4] studied the polymerization of silicic acid in hydrochloric acid solutions of pH 1-3.5. They prepared their silicic acid solution by the hydrolysis of silicon tetrachloride. Determination of the molecular weight of the silicic acid obtained by the cryoscopic method showed that it was present in the solution as disilicic acid.

When they neutralized the hydrochloric acid formed during the hydrolysis of silicon tetrachloride, the authors obtained silicic acid solutions, for which molecular weights corresponding to monosilicic acid were obtained. The pH stability regions were not identical for mono- and di-silicic acids: monosilicic acid was found to be most stable in solutions of pH 2-3, whereas disilicic acid was most stable at lower pH values, i.e., 1-2.

When solutions of the simplest acids are allowed to stand, their average molecular weight gradually rises and their diffusibility falls owing to the increase in the size and complexity of the molecules (formation of complex polymers). According to these authors the mean molecular weight of the silicic acid that reacts with albumen is higher than that of hexasilicic acid, and they introduce the idea of oligosilicic acids, by which term they describe silicic acids that are more complex than disilicic acid, but are not sufficiently complex to react with albumen. The oligosilicic acids are included in Myllius and Groschuff's α-silicic acid.

The results of the various investigations that we have cited indicate that the polymerization of silicic acid is a process that requires time and that increase in the acidity and temperature of the solution leads to an increased rate of polymerization. This process has not been subjected to quantitative investigation, and the question of the occurrence of kinetic equilibrium between the various forms of silicic acid remains obscure. There are some indications in the literature that such kinetic equilibrium may exist among the complex polymeric forms of silicic acid. Willstätter, Kraut, and Lobinger [5], for example, note that in silicic acid solutions, not only complex polymers may be present, but also more simple species. The occurrence of interconversion of one form into another is indicated by the work of Berestneva, Koretskaya, and Kargin [6], who investigated silicic acid sols by means of the electron microscope.

The question of the reversibility of the polymerization of silicic acid is of fundamental importance for its analytical determination. A study of the conditions favoring displacement of the equilibrium between the silicic acid polymers is, therefore, essential in order that an objective appraisal may be made of existing analytical procedures for the determination of silicic acid.

EXPERIMENTAL

Analytical and Experimental Procedure

In our study of the polymerization of silicic acid we have carried out a series of experiments with the object of elucidating the effect of the nature and concentration of the mineral acid, of the presence of salts, and of the duration of heating on the process. We have studied the course of the polymerization under given conditions by means of quantitative determination of the different forms of silicic acid present in the solution.

It is known that colloidal solutions of silicic acid do not react with molybdic acid with formation of the silicomolybdate complex. By the colorimetric method, therefore, we can determine only the part of the silicic acid that is present as simple molecules (or at a very early stage of polymerization). It is known also that colloidal silicic acid may be readily coagulated by the addition of coagulants and can then be separated from solution by simple filtration. Experiment has shown that the amount of silicic acid found colorimetrically in a suitably treated solution and the amount separable by treatment with gelatin are not together equal to 100% of the total amount introduced into the solution. It follows, therefore, that a suitably treated solution contains not only molecules of simple structure that react with molybdic acid and complex particles that are coagulated by gelatin, but also forms of intermediate complexity: not simple enough to react with molybdic acid, and not sufficiently complex in structure to be coagulated by gelatin.

We therefore, distinguish the following forms of silicic acid, which we classify according to the complexity of their particles: 1) α-silicic acid – various silicic acids in the early stage of the polymerization process, able to react with molybdic acid with formation of the silicomolybdate complex; 2) β-silicic acid – silicic acids that no longer react with molybdic acid, but are not yet sufficiently highly polymerized to be coagulated by gelatin; 3) γ-silicic acid – highly polymerized forms of silicic acids in which the particles are of colloidal dimensions or approach colloidal particles in complexity of structure (i.e., silicic acid sols).

We can determine α- and γ-silicic acids directly, and the content of β-silicic acid may be determined from the difference between the amount of SiO_2 taken for the experiment and the sum of the values found for the α- and γ-acids.

All three forms of silicic acid are given in the tables that follow. Comparing our classification with that proposed by Myllius and Groschuff, we see that these authors distinguish only two forms of silicic acids on the basis of molecular complexity (α- and β-forms). Myllius and Groschuff's β-form corresponds to our γ-form, and their α-form is separated in our classification into α- and β-forms, the reagent for the α-form being molybdic acid. Willstätter,

Kraut, and Lobinger regard Myllius and Grotchuff's α-silicic acid as consisting of mono-di-, and oligo-silicic acids, but they indicate no method for distinguishing experimentally between these forms.

We have investigated the polymerization of silicic acid in hydrochloric acid, nitric acid, and sulfuric acid solutions. The effect of the variation of the concentration of mineral acid was studied for acidities ranging from zero to 8 N. Over the same acidity range the effect of the presence of sodium salts on the character and rate of polymerization was investigated. The duration of heating was varied from 15 to 60 minutes.

All of the experiments described below were carried out with a standard solution of sodium silicate containing 4×10^{-3} g of SiO_2 in 1 ml of solution. The standard solution was prepared from 1 g of silica calcined to constant weight at 1100° (the purity of the silica was tested by treatment with hydrofluoric and sulfuric acids: the amount not rendered volatile by this treatment was 0.1%, and this impurity was allowed for when weighing the sample). The sample of silica was fused with five times its weight of sodium carbonate, the melt was dissolved in water, and the volume of solution was made up to 250 ml. Colorimetric determination of silicic acid in this solution showed that it was all present in the α-form. For each experiment, 20 ml of the standard solution was taken (80 mg of SiO_2). The required amount of acid was then added, and the volume of the solution was in all cases made up to 100 ml with distilled water. Heating was effected by means of boiling water: the flask containing the solution under investigation was fitted with a reflux condenser and immersed in a boiling water bath. The solution was heated for the required time and then cooled rapidly under the tap; 5 ml of solution was then taken by pipet for the colorimetric determination of silicic acid, which was based on the color of the yellow silicomolybdate complex.

The remaining solution (95 ml) was heated to 70°, and a solution of gelatin (5 ml of a 2% solution) was added. If a precipitate formed, it was allowed to settle for 10-15 minutes and then separated by filtration. The precipitate was washed on the filter with hot dilute acid (5:95), and the filter paper and precipitate were ashed and calcined at 1040-1060° to constant weight. The calcined silica was tested for purity by treatment with hydrofluoric and sulfuric acids.

Polymerization of Silicic Acid in Weakly Acid and Almost Neutral Solutions

The polymerization of silicic acid in weakly acid and almost neutral solutions prepared by addition of hydrochloric acid was investigated for pH values ranging from 7.8 to 1.2. The procedure differed from that described above in that test samples for the determination of α-silicic acid were taken during the heating process at definite intervals of time. At the end of the experiment gelatin was added to the solution in order to coagulate any γ-silicic acid that had formed, but in no case was any detected (except in the experiment in which sodium chloride was added). The 5-ml portions of solution taken for determination of the α-form were diluted in measuring flasks to 50 ml with water, and silica was determined colorimetrically in the solutions obtained. After these diluted solutions had stood for two hours, further silica determinations were made.

It was found (Table 1) that at pH 1.2 after heating for as long as two hours no polymerization of silicic acid was to be observed. The further determinations of silicic acid in the diluted solutions after standing for two hours at room temperature again revealed no polymerization. With increase in the pH of the solution (from 1.9 to 3.7) polymerization of silicic acid occurred during heating, reaching its maximum value in the first 15-30 minutes; with further heating the reverse process of depolymerization occurred, the more complex molecules being converted into simpler molecules that were able to react with molybdic acid. The further determination of silicic acid, carried out after two hours in dilute solution, also showed that in some cases reversible conversion of β- to α-form occurred.

TABLE 1

pH of solution	Amt. of α-silicic acid (% of orig. amt.) after heating for				Second determination of α-silicic acid (% of orig. amt.) after 2 hours' standing			
	15 mins.	30 mins.	1 hour	2 hours	15 mins.	30 mins.	1 hour	2 hours
1.2	102	101	102	102	100	101	101	101
1.9	80	91	89	94	82	84	92	98
3.05	91	80	89	95	–	–	–	–
3.2	93	99	101	100	91	92	96	100
3.5	81	93	97	100	90	97	98	–
3.7	92	102	101	102	102	102	101	102
7.8	54.6	50.6	44.4	50.0	59	56	48	53
7.4*	50.6	50	45.6	47.2	54	54	49	–

* Addition made of 3 g of NaCl per 100 ml of solution.

In almost neutral solutions (pH 7.8), the rate of polymerization was considerably greater: after 15 minutes' heating, almost one-half of the silicic acid present in solution had passed into the β-form and so did not react with molybdic acid and was not coagulated by gelatin. With further heating (30 minutes and one hour) polymerization continued, but the conversion of the α-form into the β-form was appreciably slower. With still further heating (two hours) the reverse process, conversion of β-form into α-form, i.e., depolymerization, was observed. The reverse process was observed also when dilute solutions were allowed to stand. The state of the system in these solutions is determined by the equilibrium $\alpha \rightleftharpoons \beta$.

The presence of appreciable amounts of sodium chloride in almost neutral solutions alters the character of the polymerization. The amount of the α-form to be found in the solution (after 15 minutes' heating) was again 50% of its initial value, but at the same time flocs of silicic acid formed in the solution. This indicated that the polymerization was going further: conversion of the β-form into the γ-form. In this case the state of the system is determined by the more complicated equilibrium $\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$. In dilute solutions containing sodium chloride, after standing or prolonged heating, the reversible conversion of the β-form into the α-form was again observed.

In order to determine the part played by the anion in the polymerization of silicic acid, experiments were carried out with solutions containing varying amounts of sodium sulfate and sodium nitrate at pH 7.3-7.7 (Table 2).

TABLE 2

Expt. No.	Salt (concentration in g/100 ml)		pH of solution	Amt. of α-silicic acid (% of orig. amt.) after heating for				Second determination of α-silicic acid (% of orig. amt.) after 2 hours' standing			
				15 min.	30 min.	1 hour	2 hours	15 min.	30 min.	1 hour	2 hours
1	$NaNO_3$	0.68	7.3	57	52.5	44.4	47	58	56	49	56
2		3.0	7.7	44	44	47	47	50	47	48	49
3	Na_2SO_4	0.5	7.5	84	81	61	45	82	45	62	51
4		3.0	7.5	93	89	61	47	99	90	65	44

In experiments with sodium nitrate in low (Expt. 1) and moderate (Expt. 2) concentration, the character and rate of polymerization were similar to those found for sodium chloride additions. Also, in presence of appreciable amounts of sodium nitrate, the formation of flocs of silicic acid was observed already after 15 minutes' heating. In the solution containing sodium sulfate in low concentration (Expt. 3), the initial rate of polymerization was considerably lower than in chloride and nitrate solutions under similar conditions, and only after two hours did the content of the α-form fall to 45%, a value close to that found in chloride and nitrate solutions. The presence of appreciable amounts of sodium sulfate (Expt. 4) delayed the conversion of the α-form into the β-form to a still greater extent in the initial stages (15 and 30 minutes), but after two hours' heating the amount of the α-form fell to 47%. In this case no flocs of silicic acid were formed; the solution merely became opalescent. In a sulfate solution, therefore, the second stage of the polymerization ($\beta \longrightarrow \gamma$) begins only after long heating of the solution.

We consider that, when a solution of sodium silicate is neutralized, the silicic acid formed undergoes a process of polymerization:

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3;$$

$$nH_2SiO_3 = H_{2m}Si_nO_{(2n+m)} + (n-m)H_2O,$$

in which $m < n$, and the value of n rises as polymerization proceeds, i.e., the silicic acid molecules become larger and more complex.

Our results indicate that the polymerization of silicic acid is a reversible process. In presence of salts and with rise in temperature the equilibrium is displaced to the right, i.e., the formation of polymeric forms of silicic acid is facilitated. On the other hand, presence in the solution of small amounts of acid (pH 1) leads to displacement of the equilibrium to the left, i.e., promotes the reverse process, depolymerization.

Polymerization of Silicic Acid in Acid Solutions

Hydrochloric Acid Solutions. The effect of variation in the concentration of hydrochloric acid was investigated over the range 1.4 N to 8 N. The effect of the duration of heating on the polymerization was investigated for the times 15, 30, and 60 minutes. The results obtained are illustrated in Figures 1, 2, and 3. Each point on the graphs represents a mean value, obtained from the results of a number of parallel experiments. The divergence between the values found in parallel experiments for the contents of α- and γ-silicic acids did not generally exceed 1-2%;

cases in which lower reproducibility was found are given special mention in the text.

From these results it will be seen that after 15 minutes' heating (Fig. 1), no polymerization is to be observed in a solution containing 5% HCl* (1.37 N): colorimetric determination shows that the whole of the silicic acid in the solution is present in the α-form. Even at an acidity of 2 N, practically no polymerization is to be observed under these conditions of heating.

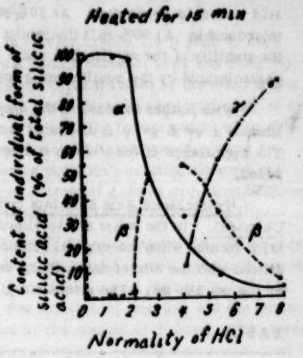

Fig. 1

When the concentration of HCl is increased to 10% (2.7 N), already after 15 minutes' heating only 50% of the initial amount of acid is in the α-form: the remainder is in the form of larger molecules, but these have still not attained sufficiently large dimensions to be coagulated by gelatin. In this case the state of the system is determined by the equilibrium $\alpha \rightleftharpoons \beta$. The divergence between the amounts of α-form found in parallel experiments is 5% (48% and 53%); this indicates an unstable state of equilibrium between α- and β-forms.

When the concentration of HCl is further increased to 15% (4 N), only 33% remains of the simplest form of silicic acid, and at the same time a third form, γ-silicic acid, is found to be present. The rate of conversion of the β- into the γ-form is less than the rate of conversion of the α- into the β-form. The solution, therefore, contains an appreciable amount of the intermediate β-form. The state of the system has become more complex, being determined by the equilibrium between three forms: $\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$.

When the concentration of HCl is still further increased, the contents of α- and β-forms fall, and that of the γ-form rises. At 30% HCl (8 N), the mean value for the content of α-form is 4%, and the main form present is γ-silicic acid. We must point out that for this HCl concentration, whereas repeat experiments show satisfactory reproducibility for the α-form, a considerable variation is found for the γ-form (76.7-94.5%), which is reflected in the figures obtained, by difference, for the β-form. This indicates high lability in the equilibrium between β- and γ-forms and indefiniteness in the boundary between these forms.

Longer heating under the same conditions (30 minutes' heating; Fig. 2) results in practically no polymerization at relatively low concentrations of HCl, as in the case of the 15-minute experiments. When the concentration of HCl

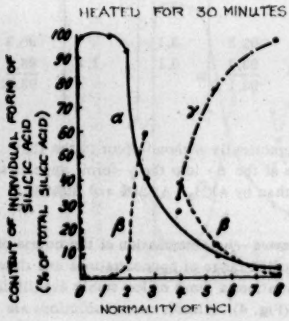

Fig. 2

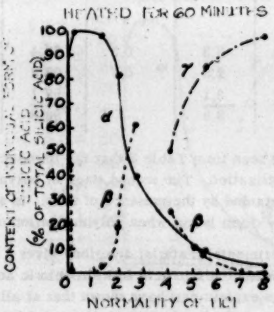

Fig. 3

is increased, the polymerization goes further than in the corresponding experiments at the shorter time of heating. Hence, when the duration of heating is increased, other conditions remaining constant, the equilibrium is displaced

* Here and later the concentration of acid is expressed in grams per 100 ml of solution.

in the direction of the formation of more complex particles. At HCl concentrations of 15% and higher, γ-silicic acid makes its appearance. At 20% HCl the content of the γ-form increases sharply, but the values found are poorly reproducible. At 30% HCl the results for the determination of α- and γ-forms are highly reproducible, indicating the stability of the equilibrium under these conditions, but the β-form is almost absent, and the system is, therefore, characterized by the equilibrium $\alpha \rightleftharpoons \gamma$.

With further increase in the duration of heating (Fig. 3), essentially the same picture is presented. The equilibrium $\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$ is displaced somewhat more in the direction of the formation of more higly polymeric forms. The appearance of the γ-form is observed already at 10% HCl, for the solution becomes opalescent when gelatin is added.

Hydrochloric Acid Solutions containing an Appreciable Amount of a Salt (Sodium Chloride or Aluminum Chloride). In the series of experiments described above, the solutions contained only small amounts of sodium salts, formed when the original solution was acidified. Special experiments were carried out under the same conditions with the aim of determining the effect of large amounts of NaCl (up to 3 g per 100 ml) and of $AlCl_3$ (up to 80 mg per 100 ml). The results are given in Table 3.

TABLE 3

Concentration of HCl		Amount of various forms of silicic acid (% of total amount) after heating solution for 30 minutes								
					in presence of NaCl			in presence of $AlCl_3$		
(N)	(g/100 ml)	α	β	γ	α	β	γ	α	β	γ
0	0	50.6	49.4	–	50	–	–			
1.37	5	97.5			98.1			93.8		
		100.0	1.2	–	95.6	3.2	–	96.2	5	–
		98.8			96.8			95		
		40.0			38.8			42.5		
2.74	10	41.2	59.4		37.5	61.9	–	38.8	59.4	–
		40.6			38.1			40.6		
							64.6	9.4		67.0
							76.0	10.0		72.3
		9.7		71.3	8.8		74.0	9.7		72.1
5.48	20	9.4	14.6	80.4	8.1	18.8	71.7	8.8	20.3	70.2
		9.5		75.9	10.9		71.6	9.5		
					10.6					
					9.6					
		3.3	0.3	96.4	3.7		92.5	3.1		95.3
8.22	30	2.5	0.7	96.8	3.1	3.5	93.7	3.1	1.1	96.0
		3.1		97.1	3.4		93.1			95.65
		3.0		96.8						

It will be seen from Table 3 that the introduction of NaCl or $AlCl_3$ is practically without effect in the first stage of polymerization. The second stage of polymerization, the conversion of the β- into the γ-form, appears to be somewhat retarded by the presence of salts: to a greater extent by NaCl than by $AlCl_3$. At 20% and 30% HCl, the content of γ-form is less when polymerization occurs in presence of salts.

The experimental material described gives a sufficiently clear quantitative characterization of the course of the polymerization of silicic acid in hydrochloric acid solutions within the studied range of concentrations and times of heating. The experiments have shown that at all of the given HCl concentrations a more or less stable equilibrium between the various forms of silicic acid is established in the course of time (Fig. 4). Almost neutral solutions are exceptional: in this case there is a rapid fall in the content of α-silicic acid to 50-54% of its initial value, and as the duration of heating is increased, a stable equilibrium between the α- and β-forms is not established (Fig. 4).

In very weakly acid solutions (pH 1.9-3.7), at first (after 15-30 minutes' heating) there is a relatively small fall in the content of α-form (to 80% of the initial value), but with further heating the reverse process of depolymerization prevails, and the content of α-form increases and approaches its initial value. At pH 1.2, i.e., in a more acid solution, no polymerization at all is to be observed, even after heating for two hours. When the acidity is still further

increased to 1.4 N, the picture remains almost unchanged: there is a very slight fall in the content of α-form with time. The acidity range 0.1-1.0 N must, therefore, be regarded as the most favorable for the stable existence of silicic acid in its simplest form (within the limits of the period of time studied).

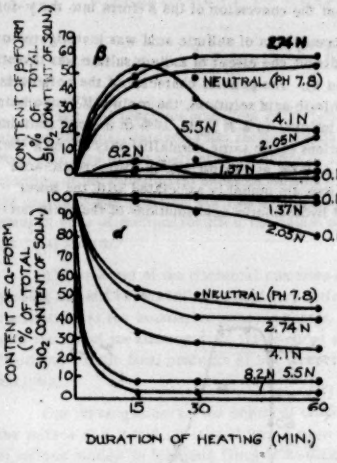

Fig. 4

Further increase in acidity beyond 1.4 N leads to polymerization of silicic acid, which becomes more and more pronounced as the acidity rises. This is shown by the rapid fall in the content of the α-form in the first period (15 minutes) of the heating, and by the slower fall in the further period of heating. In the acidity range 2-4 N, equilibrium between α- and β-forms is not attained during one hour's heating, although the curve for the variation of content of α-form with time becomes more and more nearly horizontal after 30 minutes' heating.

For acidities of 5.5-8 N the content of α-form is already much less after 15 minutes' heating, and then remains constant during further heating (parts of the curves that are parallel to the axis of abscissas). For acidities of less than 4 N the content of α-form is determined by the content of β-form. The curves for the variation of the contents of α- and β-forms with time form mirror images of one another: the equilibrium is determined by the concentrations of α- and β-forms. At acidities of greater than 4 N the content of β-form falls as it passes into the γ-form, and at 8 N the β-form is practically absent. The equilibrium of the system is apparently determined by equilibrium between simple and polymeric forms: $\alpha \rightleftharpoons \gamma$.

Nitric Acid Solutions. The effect of variation of the concentration of nitric acid on the polymerization of silicic acid was investigated over the same range of acidity, 0.8-8 N. The duration of heating was varied from 30 to 60 minutes. Also, the effect of sodium nitrate on the course of the polymerization process was examined under the same conditions. Comparison of the results (Figs. 5 and 6) with those obtained for hydrochloric acid solutions shows that in general character the processes are similar; nitric acid solutions, however, show a number of differences that are of interest.

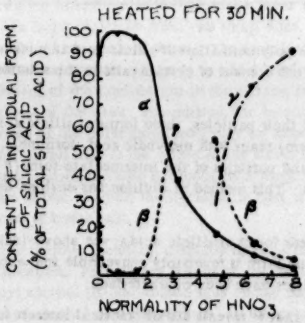

Fig. 5

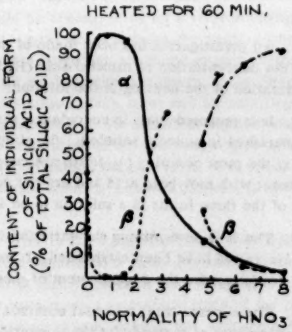

Fig. 6

1. In nitric acid solutions of medium concentration (3-4 N) the content of the α-form is somewhat greater after 30 minutes' heating than in hydrochloric acid solutions under the same conditions, i.e., the first stage of the polymerization, the conversion of the α-form into the β-form, proceeds somewhat more slowly; increase of the duration of heating to one hour reduces the difference. When the HNO_3 concentration is increased to 5 N this retardation of the first stage of the polymerization is no longer observed.

2. The second stage of the polymerization, the conversion of the β-form into the γ-form, is slower in nitric acid solutions, and in 8 N HNO_3 some β-form is still present, whereas in 8 N HCl it cannot be detected.

3. In general, the presence of sodium nitrate in nitric acid solutions has no effect on the polymerization of silicic acid; only in a definite range of acidity (4-5.5 N) does it retard the conversion of the β-form into the γ-form.

Sulfuric Acid Solutions. The effect of the variation of the concentration of sulfuric acid was investigated over the acidity range 1-8 N, heating being for 30 and 60 minutes. In addition, the effect of sodium sulfate was investigated for the same range of concentrations of sulfuric acid (Figs. 7 and 8). The general character of the polymerization of silicic acid in sulfuric acid solutions is the same as in hydrochloric acid solutions, the main difference being that the process is slower than in hydrochloric acid and nitric acid solutions. In 8 N H_2SO_4 10% of α-form remains after one hour's heating, whereas in hydrochloric and nitric acid solutions of the same normality only 3% of α-form is to be found. Correspondingly, the content of γ-form in 8 N H_2SO_4 is 90%, as against 97% in hydrochloric acid solution. These peculiarities of polymerization in sulfuric acid solutions are probably associated with the lower activity of hydrogen ions, in comparison with that found in nitric and hydrochloric acid solutions of the same normality.

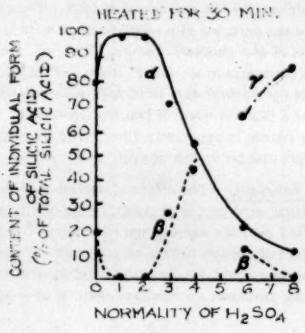

Fig. 7

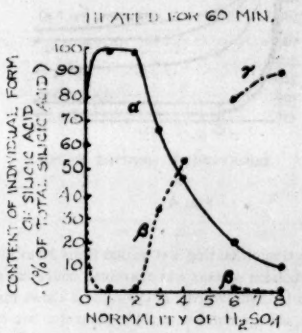

Fig. 8

SUMMARY

1. An investigation has been made of the dependence of the polymerization of silicic acid in aqueous solution on the concentration of mineral acid (HCl, HNO_3, H_2SO_4), on the content of certain salts in the solutions, and on the duration of the heating of the solution.

2. It is proposed that, in accordance with the complexity of their particles, three forms of silicic acid should be distinguished in aqueous solution: the simplest particles (α-form) react with molybdic acid, forming a colored complex; the most complex (γ-form) are coagulated by gelatin; and particles of the intermediate form (β-form) do not react with molybdic acid and are not coagulated by gelatin. This method of division has enabled the content of each of the three forms in a solution to be determined.

3. The laws determining the variation in the contents of these forms of silicic acid as the above-indicated factors are varied have been established. It has been shown that one form is reversibly convertible into another, and the conditions for the displacement of these equilibrium processes have been characterized.

4. The experimental material obtained and the regularities that it reveals are of practical interest for scientific development of methods for the separation of silicic acid from solutions.

Received December 3, 1952

Institute of Silicate Chemistry of the USSR Academy of Sciences

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DISPLACEMENT OF CHEMICAL EQUILIBRIUM IN A SURFACE LAYER

S. E. Bresler and G. V. Samsonov

Chemical processes occurring at the boundary between two phases have been well studied from the point of view of kinetics: this study has formed the basis of a whole science – heterogeneous catalysis. Much attention has been paid also to the study of the kinetics of chemical processes occurring in insoluble films on liquid surfaces. The question of the equilibrium between substances reacting in the surface layer has not yet attracted attention; usually, the reactants and products, e.g., in heterogeneous catalysis, are found in the same phase, and therefore, from the point of view of thermodynamics, the course of the process in the surface layer has no effect on the composition of the final system.

The problem of the chemical processes occurring in a surface layer may be solved in a different way: by regarding substances remaining in boundary surface as products. The question then arises of the conditions of chemical equilibrium at the boundaries between phases. The experimental investigation of this question may be carried out with the aid of measurements of the physical properties of the reacting system or by a method depending on the "freezing" of the final products at low temperature, their transference into a homogeneous phase, and chemical analysis.

Our investigations on the course of chemical processes have been carried out in an insoluble film, formed on the surface of a liquid. It is well known from experiments with the Langmuir balance that the maximum lowering of surface tension in insoluble films is 30-40 dynes/cm. This lowering can be interpreted as a supplementary pressure created by the mono-layer on an area of length 1 cm and width equal to the length of the molecules oriented in the surface layer. It is easy to see, therefore, that the excess pressure in a surface layer may attain 200 or more atmospheres, sufficient to cause an appreciable displacement of chemical equilibrium in condensed systems, if the volume change in the chemical process is not too small and the free energy of the process is not too great. A favorable process from this point of view is the synthesis of esters from acids and alcohols. The esterification process should not occur in presence of the large mass of water in contact with the molecules of the surface layer, since water is produced in this reaction.

The free energy of the formation of esters from fatty acids and alcohols is $\Delta F = 900$ cal/mole [1]. The volume change during esterification in the surface layer is made up of two parts: the loss of water molecules and the formation of one large molecule from two small ones. Such processes should be accompanied by a volume change of not less than 20 ml per mole of ether. The associated external work $\Delta F' = p\Delta v$, which reduces the positive free energy of the chemical process, amounts to a few hundred calories. Under these conditions we might expect an appreciable displacement of the equilibrium in the surface layer, as compared with the homogeneous phase, in the direction of the synthesis of the ester. In addition, the orientation of the molecules in the surface layer and the resulting partial dehydration of the polar group may play an important part in the displacement of the chemical equilibrium. We may refer to this also as the effect of the steric factor: owing to the orientation of the ester molecules (when, as experiment shows, the area occupied by a molecule is 21 A^2 and the hydrocarbon radicals form, as it were, continuations of one another) the hydrophilic part of the molecule is removed from the aqueous phase, and this hinders the process of hydrolysis.

Both factors, therefore, displace the equilibrium in the surface layer in the same direction: from hydrolysis to esterification. Preliminary results on the formation of an ester in the surface layer from myristic acid and hexadecyl alcohol [2] were based only on the measurement of the fall in surface pressure after bringing a mixture of acid and alcohol onto the surface. In the present investigation we have made a systematic study of the process of esterification of various organic acids and alcohols both by the Langmuir-Adam method, and with the aid of microchemical colorimetric analysis.

EXPERIMENTAL PROCEDURE

The esterification process was studied for a series of organic acids – from lauric to palmitic – reacting with hexadecyl or octadecyl alcohol in monomolecular surface films formed on a water surface in a Langmuir trough. In carrying out the work all essential precautions were taken: the trough, covered with pure paraffin, was contained in a glass-covered box; two-way movement of the barrier was effected by remote control with the aid of nuts actuated

by a threaded rod attached to the wall of the box; the threaded rod was rotated by means of an electric motor, which was supported independently in order to avoid disturbance to the surface of the liquid. The surface tension (pressure) was measured by the detachment method, using a torsion balance and a glass plate having a perimeter of 20 mm. As all of the work was carried out with condensed films, a highly sensitive balance was not necessary. The probable error in the measurement of surface tension was 0.25 dyne/cm. For the formation of the film, a 0.1% solution of the acid and alcohol in hexane (distilled through a column) was used. The solution was applied in the form of 5-6 drops (total volume about 0.1 ml) from a specially calibrated micropipet. Removal of the film for analysis was carried out by two methods: transfer of the monomolecular layer to a solid metal plate [3], and decantation of the top layer of liquid, together with the film, into a special vessel. The first method gave the most reproducible results.

The esters formed in the films were extracted from the trough as described and subjected to chemical analysis. Since the total amount of acid and alcohol placed on the surface was only about 0.1 mg, and the amount of ester formed was still less, we selected the colorimetric method for the determination of esters by the hydroxamic reaction [4], which permits the determination of hundredths of a milligram of ester. The hydroxamic acid formed by the reaction of an ester and hydroxylamine in absolute ether

$$R_1COOR_2 + NH_2OH \rightarrow R_1CONHOH + R_2OH$$

gives a red complex with ferric salts:

$$3R_1CONHOH + FeCl_3 \rightarrow (R_1CONHO)_3Fe + 3HCl.$$

The extinction coefficients of the colored solutions were measured with a Soviet SF-1 spectrophotometer. The absorption curves of standard solutions of butyl oleate are given in Fig. 1. Fig. 2 shows the dependence of the extinction coefficient at 525 mμ on the concentration; it follows the Lambert-Beer law with great accuracy.

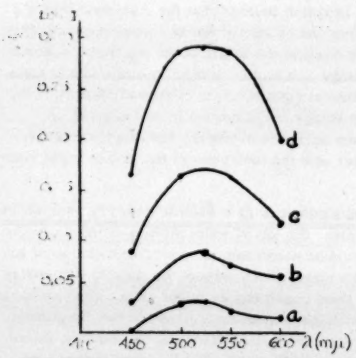

Fig. 1. Absorption curves for solutions of butyl oleate after formation of the hydroxamic complex: a) for $c = 0.185 \cdot 10^{-3}$ mM; b) for $c = 0.745 \cdot 10^{-3}$ mM; c) for $c = 1.78 \cdot 10^{-3}$ mM; d) for $c = 3.00 \cdot 10^{-3}$ mM

Our investigations have shown that the reproducibility of the results is not high when esters derived from acids having more than ten carbon atoms and alcohols of similar molecular size are analyzed by the method described. The presence of water in the ester solution has a considerable effect in these cases. Tolerable results can be obtained

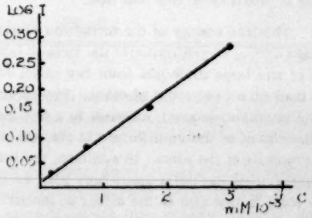

Fig. 2. Dependence of extinction coefficient on concentration.

only by long boiling of a solution of the ester and hydroxylamine in diethyl ether. The explanation of this difficulty may lie in the low solubility of the esters. For this reason we modified our procedure, carrying out the whole process of preparing the hydroxamic acid in absolute pentane, in which water is practically insoluble.

Results of the spectrophotometric investigation of the hydroxamic complex obtained from hexadecyl myristate in pentane are given in Figs. 3 and 4. The straight lines in Figs. 2 and 4 can be satisfactorily superposed, and this gives us reason to suppose that we may determine the concentration of any of the esters obtained from the same calibration curve when very high accuracy is not required. The hexadecyl myristate required for the construction of the calibration curve was synthesized by us from myristoyl chloride and hexadecyl alcohol and was recrystallized several times.

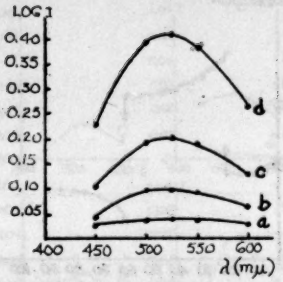

Fig. 3. Absorption curves for solutions of hexadecyl myristate after formation of the complex: a) for $c = 0.456 \cdot 10^{-3}$ mM; b) for $c = 1.14 \cdot 10^{-3}$ mM; c) for $c = 2.28 \cdot 10^{-3}$ mM; d) for $c = 4.56 \cdot 10^{-3}$.

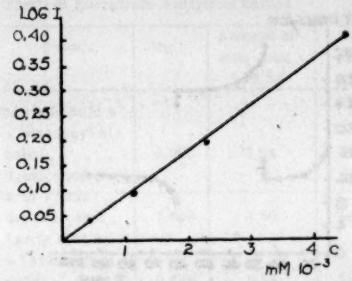

Fig. 4. Spectrophotometric curve for the hydroxamic complex formed from cetyl myristate in pentane.

Experiments on the Method of Determining Surface Pressure

The simplest method of observing chemical reactions in a surface layer covering a liquid is by measurement of the surface tension (surface pressure). We first studied the stability of films formed by the starting substances: lauric, tridecanoic, myristic, and palmitic acids, and hexadecyl and octadecyl alcohols. Films were formed with amounts of substance calculated to provide one molecule to each 25 A^2 of surface, and surface tension measurements were made at ten-minute intervals over a period of 3-5 hours. When films were formed on water, only the alcohols and palmitic acid gave fully stable films. When 0.02 N HCl was used, all of the films were found to be sufficiently stable with the exception of lauric and tridecanoic acid films. The acidity of the water phase reduced the dissociation of the fatty acids, and so reduced their solubility and stabilized the film. All further work was done on 0.02 N HCl. In the experiments on esterification, the amount of an equimolecular mixture of acid and alcohol necessary to provide one molecule for each 25 A^2 of surface was placed on the surface of 0.02 N HCl contained in the trough.

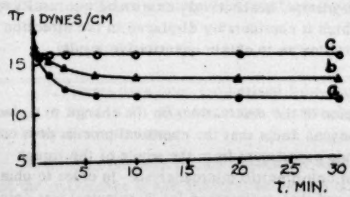

Fig. 5. Variation of surface pressure: a) myristic acid + hexadecyl alcohol; b) palmitic acid + hexadecyl alcohol; c) myristic acid + octadecyl alcohol.

The results of surface pressure measurements in the systems myristic acid + hexadecyl alcohol, palmitic acid + hexadecyl alcohol, amd myristic acid + octadecyl alcohol are given in Fig. 5. In the first and last systems there was an appreciable fall in surface pressure with time; it was substantially complete in one hour. No such effect was observed in the second system. We considered that palmitic acid formed a solid film at room temperature and could not react with the alcohol owing to the low mobility of its molecules. Experiments at 38° showed that under these conditions palmitic acid itself did not give a stable film owing to partial dissolution, so that a study of the kinetics of esterification could not be made from observations on the fall in surface pressure. However, synthesis of hexadecyl palmitate can be proved beyond doubt by means of chemical analysis.

Control experiments with surface films containing only acid or only alcohol showed (when stable films were obtained) that, when the substances were applied from hexane, the surface tension was established in 1-3 minutes, and then remained unchanged for several hours. As we considered that the surface pressure itself plays an important part in the displacement of chemical equilibrium, we carried out experiments in which we observed the change in surface pressure after compression and extension of the film, effected by movement of the barrier (Figs. 6 and 7). Both in the system myristic acid + hexadecyl alcohol and also in the system myristic acid + octadecyl alcohol, after each compression of the film (increase in surface pressure) a new gradual fall in surface pressure was observed, which occupied about ten minutes. After extension of the films the reverse phenomenon occurred: the surface pressure

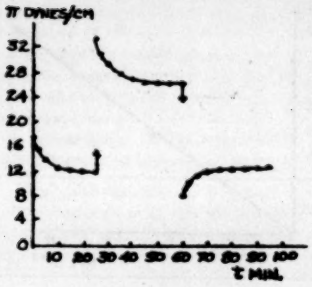

Fig. 6. Change in surface pressure after compression and extension of films in the system myristic acid + + hexadecyl alcohol.

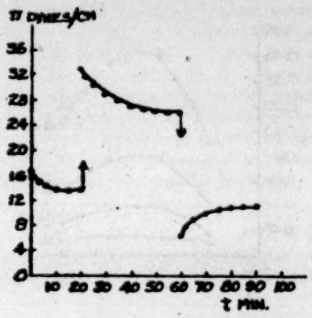

Fig. 7. Change in surface pressure after compression and extension of films in the system myristic acid + + octadecyl alcohol.

gradually rose. Our explanation of the observed phenomena is as follows: when the surface pressure is raised, further synthesis of ester occurs owing to a displacement in the equilibrium, and when the pressure is reduced the opposite process, ester hydrolysis, occurs. The control experiments with pure acids and alcohols indicated the insignificance of effects due to elastic after-effects, which cannot in any way eliminate the result obtained.

A study of the reverse process of ester hydrolysis, and particularly of the attainment of equilibrium from this side, would be of interest, but the films obtained by applying hexadecyl myristate to the surface of water were found to be fragile and of low stability: they exist for only a very short time and are broken down as soon as they are subjected to an insignificant pressure from the movable barrier. Experiments with hexadecyl myristate, and also with the ternary system myristic acid + hexadecyl alcohol + hexadecyl myristate, qualitatively confirmed our results on the existence of an equilibrium in this system in the surface film which is considerably displaced in the direction of ester synthesis. However, the low stability of the ester films did not allow us to obtain quantitative results.

Results of Chemical Analysis

Although there may still be some ambiguity in the interpretation of the observations on the change in surface pressure, the direct chemical analysis of the esters obtained shows beyond doubt that the chemical process does occur. As our preliminary results showed, the amount of ester obtained in one experiment from the whole of the trough (600 sq.cm) is insufficient even for an extremely sensitive method of colorimetric microanalysis. In order to obtain a larger amount of product, the film (formed from acid and alcohol and then maintained for 30 minutes) was compressed, and a glass plate having raised edges was introduced below it; the film, together with the top layer of liquid, was then transferred to a vessel contained in a Dewar flask containing liquid air (to freeze the equilibrium). This operation was repeated ten times for each system, and all the organic substances were then extracted from the water (after thawing) by means of pentane, and analysis for the content of ester was carried out by the hydroxamic method. The results of the spectrophotometric analysis of the hydroxamic complex in the systems lauric acid + hexadecyl alcohol, tridecanoic acid + hexadecyl alcohol, myristic acid + hexadecyl alcohol, and palmitic acid + hexadecyl alcohol (18° and 38°) are given in Fig. 8. The yield of ester in the surface layer may attain 20% (see Table).

The results obtained could only be convincing after numerous control experiments. With this object water films (0.02 N HCl), after remaining in the trough for a sufficient period of time, were analyzed in order to make sure that esters in micro amounts did not separate from the paraffin. Similar control experiments were carried out with films of fatty acids and alcohols. Each substance was separately applied to the surface of the solution in the trough. All these control experiments showed that the finding of ester in the synthesis experiments could not result from the contamination of the paraffin or the original acids and alcohols. There still remained the question of the possibility of the formation of esters after thawing of the pentane solutions. Experiments showed that mixtures of aliphatic alcohols and acids do not yield even traces of esters in the course of one day, when dissolved in pentane

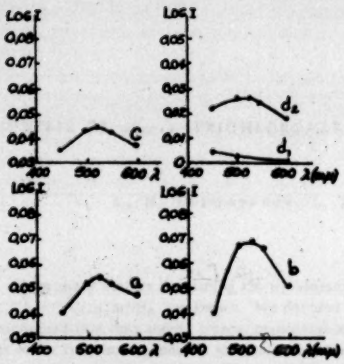

Fig. 8. Curves for the spectrophotometric investigation of the hydroxamic complex in the systems: a) myristic acid + hexadecyl alcohol; b) tridecanoic acid + hexadecyl alcohol; c) lauric acid + hexadecyl alcohol; d) palmitic acid + hexadecyl alcohol (d_1 at 18°, d_2 at 38°).

TABLE

Yields of Esters from Analytical Results

System	log I	Amount of ester (mM · 10^{-3})	Yield (%)
Myristic acid + + hexadecyl alcohol	0.055	0.64	16
Tridecanoic acid + hexadecyl alcohol .	0.069	0.80	20
Lauric acid + + hexadecyl alcohol	0.045	0.54	14
Palmitic acid + hexadecyl alcohol at 38° . . .	0.026	0.32	8

containing a small amount of acid (the pentane was first brought into equilibrium with 0.02 N HCl in a separating funnel).

This shows that not only the conditions for equilibrium, but also the rate at which equilibrium is attained, is different in the surface film than in the bulk of the solution, which, of course, is fairly well known to be so. The direct chemical experiment, therefore, was found to be in full accord with observations made by the Langmuir-Adam method. The occurrence of the synthesis of an ester from a fatty acid and an alcohol under the conditions existing in a monomolecular layer is proved. This proves also that under the conditions found in a monomolecular layer a dehydration reaction occurs in presence of a practically infinite reservoir of water; in other words, the peculiar conditions existing in the surface layer displace the chemical equilibrium from hydrolysis to synthesis.

SUMMARY

1. Esters have been synthesized from organic acids and alcohols in a monomolecular layer on the surface of water (0.02 N HCl). The formation of esters has been proved by a microchemical analytical method and also by the fall in surface pressure.

2. The synthesis occurs in presence of the enormous amount of water that supports the film. The possibility of the occurrence of the dehydration process is associated with the peculiar conditions that are found in the surface layer.

The effect of surface pressure on the displacement of chemical equilibrium in a monomolecular layer has been demonstrated.

Received February 21, 1953.

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SYNTHESIS OF ω,ω,ω-TRICHLOROALKYLAMINES AND ω,ω-DICHLOROALKENYLAMINES

A. N. Nesmeyanov, L. I. Zakharkin, and R. Kh. Freidlina

No primary amines containing the trichloromethyl or 2,2-dichlorovinyl group and of the types $CCl_3(CH_2)_nNH_2$ and $CCl_2 = CH(CH_2)nNH_2$, are known. We decided to carry out the synthesis of such bifunctional compounds, since we considered that they should present considerable interest from the point of view of their reactivity, the mutual effect of the functional groups in the molecule, and so on [1, 2]. We hoped to effect the synthesis of compounds of these structures containing odd numbers of carbon atoms by the ammonolysis of α,α,α,ω-tetrachloroalkanes and α,α,ω-trichloroalkenes. α,α,α,ω-Tetrachloroalkanes are quite accessible substances, being prepared by the addition of carbon tetrachloride to ethylene with application of heat and pressure in presence of various initiators. Trichloroalkenes of structure $CCl_2 = CH(CH_2)_nCl$ are readily prepared by the elimination of hydrogen chloride from these tetrachloroalkanes [3]. The synthesis of amines of the above types containing an even number of carbon atoms we hoped to bring about by the hydrogenation of nitriles, which would have to be obtained by the action of potassium or sodium cyanide on the corresponding tetrachloroalkanes or trichloroalkenes.

The action of ammonia on α,α,α,ω-tetrachloroalkanes has not been studied. It was thought that this reaction might be complicated by the fact that a highly nucleophilic reagent, such as ammonia, can attack the tetrachloroalkane molecule both at the carbon atom carrying one chlorine atom, and at the carbon atom carrying three chlorine atoms. Treatment of 1,1,1-trichloropentane with ammonia in a methanol medium at 145-150° for ten hours showed, however, that the trichloromethyl group is inert with respect to the action of ammonia under these conditions. 1,1,1,5-Tetrachloropentane, on being heated with ammonia in alcoholic solution, yielded 5,5,5-trichloropentylamine in satisfactory yield. 5,5-Dichloro-4-pentenylamine was formed as a by-product in this synthesis, and, in addition, resin formation occurred. The reaction between 1,1,1,7-tetrachloroheptane and ammonia did not go quite as well: the yield of the corresponding unsaturated amine approximated to that of 7,7,7-trichloroheptylamine, and there was also more resin formation. It was not found possible to obtain the trichlorononylamine from 1,1,1,9-tetrachlorononane and ammonia.

The reaction between α,α,ω-trichloroalkenes and ammonia went considerably better: it was found possible to obtain not only 5,5-dichloro-4-pentenylamine and 7,7-dichloro-6-heptenylamine, but also 9,9-dichloro-8-nonenylamine, the yields of the three substances being 73%, 58%, and 50% respectively.

The hydrogenation of nitriles containing a trichloromethyl or 2,2-dichlorovinyl group has not been studied. There is little information available also about the hydrogenation of other compounds containing the trichloromethyl group. We may, however, refer to a short communication [4] regarding the reduction of 1,1,1-trichloro-3-nitro-2-alkanols into the corresponding aminotrichloroalkanols by means of hydrogen in presence of Raney nickel in an absolute alcohol medium. Unfortunately, the authors have not published a more detailed paper on this subject. A patent [5] has appeared recently on the hydrogenation of polyhalo compounds containing a trichloromethyl group by means of hydrogen in presence of a platinum catalyst and a base for binding the hydrogen chloride formed. The reaction occurring under these conditions may be represented as follows:

$$2R-CCl_3 \xrightarrow[Pt]{H_2,\ NH_3} R-CCl_2-CCl_2-R \xrightarrow[Pt]{H_2,\ NH_3} RCH_2CH_2R,$$

where R is a hydrocarbon or halohydrocarbon residue.

By the hydrogenation of 6,6-dichloro-5-hexenenitrile under pressure in presence of Raney nickel in a methanol medium, the corresponding dichlorohexenylamine was isolated in low yield, and at the same time a small fraction of a lower-boiling fraction was obtained. It is possible that the low yield of product and the presence of

by-products are associated with the hydrogenation of the 2,2-dichlorovinyl group and with the replacement of a chlorine atom by hydrogen in presence of the base formed as a result of the hydrogenation of the cyano group. Carrying out the reaction under the same conditions, but in presence of 1,1,1,5-tetrachloropentane, which should act as a chlorine donor, led to the preparation of 6,6-dichloro-5-hexenylamine, and although a poor yield was obtained, there were no by-products, as the low-boiling substances were not formed under these conditions.

Hydrogenation of 6,6,6-trichlorohexanenitrile in a methanol medium in presence of Raney nickel led to the formation of 6,6-dichlorohexylamine, but not 6,6,6-trichlorohexylamine. We therefore carried out the synthesis of 6,6,6-trichlorohexylamine according to the following scheme:

$$CCl_3(CH_2)_4Cl + NaHC(COOC_2H_5)_2 \longrightarrow CCl_3(CH_2)_4CH(COOC_2H_5)_2 \xrightarrow[HCl]{H_2O} CCl_3(CH_2)_5COOH \xrightarrow{HN_3}$$

$$\longrightarrow CCl_3(CH_2)_5NH_2.$$

All the amines that we have prepared are colorless liquids having a specific amine odor and distillable under reduced pressure. Trichloroalkylamines resinify appreciably on standing, and in the case of 5,5,5-trichloropentylamine, the hydrochloride of the original trichloropentylamine was isolated from the resinified mass. Dichloroalkylamines and dichloroalkenylamines are stable to storage. All the amines obtained form crystalline benzoyl derivatives when treated with benzoyl chloride. It is interesting to note that the benzoyl derivatives of the trichloroalkylamines containing an odd number of carbon atoms melt higher than the corresponding benzoyl derivative of the trichloroalkylamine containing an even number of carbon atoms. The same is observed also for the melting points of the benzoyl derivatives of the dichloroalkenylamines, as will be seen from the table.

TABLE

Benzoyl derivative	M.p. (°C)	Benzoyl derivative	M.p. (°C)
$CCl_3(CH_2)_4NHCOC_6H_5$	95-96	$CCl_2=CH(CH_2)_3NHCOC_6H_5$	55-56
$CCl_3(CH_2)_5NHCOC_6H_5$	70.5-71.5	$CCl_2=CH(CH_2)_4NHCOC_6H_5$	36-37.5
$CCl_3(CH_2)_6NHCOC_6H_5$	91-92	$CCl_2=CH(CH_2)_5NHCOC_6H_5$	37.5-38
		$CCl_2=CH(CH_2)_6NHCOC_6H_5$	—
		$CCl_2=CH(CH_2)_7NHCOC_6H_5$	44.5-45.5

EXPERIMENTAL

5,5-Dichloro-4-pentenylamine

A solution of 25 g of 1,1,5-trichloro-1-pentene in 100 ml of methanol containing 12 g of ammonia was heated in a steel ampoule at 80-85° for eight hours. The methanol and ammonia were then driven off in a water bath. Dilute hydrochloric acid was added to the residue, and the oil remaining undissolved was extracted with ether. The hydrochloric acid solution was cooled and made alkaline with a solution of caustic soda. The base that separated was extracted with ether, and the extract was dried with sodium sulfate. 5,5-Dichloro-4-pentenylamine (16.2 g, 73%) came over at 68-69° (7 mm); it had n_D^{20} 1.4899; d_4^{20} 1.1736; Found MR 37.98; Calculated MR 37.93.

	Found %:	N 9.22, 9.44
$C_5H_9Cl_2N$.	Calculated %:	N 9.09

Its benzoyl derivative melted at 55-56° (from ligroin).

	Found %:	N 5.50, 5.56
$C_{12}H_{13}Cl_2ON$.	Calculated %:	N 5.42

6,6-Dichloro-5-hexenenitrile

A mixture of 62 g of 1,1,5-trichloro-1-pentene, a solution of 32 g of potassium cyanide in 55 ml of water and 150 ml of ethanol, and 3 g of sodium iodide was heated with stirring for ten hours. The alcohol was then distilled off, and water was added to the residue to dissolve the salts. The oil present was extracted with chloroform, and the chloroform solution was washed once with water and dried with calcium chloride. Vacuum distillation yielded 13 g of the original trichloropentene and 42 g (72%) of 6,6-dichloro-5-hexenenitrile, b.p. 80-81° (3 mm), n_D^{20} 1.4815;

d_4^{20} 1.2018; Found MR 38.87; Calculated MR 38.99.

Found %: N 8.57, 8.34

$C_6H_7Cl_2N$. Calculated %: N 8.54

6,6-Dichloro-5-hexenylamine

A solution of 35 g of 6,6-dichloro-5-hexenenitrile and 35 g of 1,1,1,5-tetrachloropentane in 100 ml of methanol was hydrogenated in presence of 5 g of Raney nickel and hydrogen at 100 atm at 75° for three hours. After removal of the catalyst, the methanol was distilled off in a water bath. Dilute hydrochloric acid was added to the residue, and the undissolved part was extracted with chloroform. The hydrochloric acid solution was cooled and treated with a solution of caustic soda, when separation occurred of the free amine and also of nickel hydroxide, which had to be removed by filtration. The amine was extracted with ether, and the extract was dried with sodium sulfate. The dichlorohexenylamine (7.8 g, 22%) distilled over at 83-84° (6 mm); it had n_D^{20} 1.4865; d_4^{20} 1.1331; Found MR 42.61; Calculated MR 42.61.

Found %: N 8.56, 8.54

$C_6H_{11}Cl_2N$. Calculated %: N 8.33

Fractionation of the chloroform solution yielded 15 g of the original dichlorohexenenitrile. The dichlorohexenylamine, on being hydrolyzed with sulfuric acid, yielded 6-aminohexanoic acid, m.p. 200-201°, identified by determination of the melting point of a mixture of the substance with an authentic sample.

The benzoyl derivative melted at 36.5-37.5° (from ligroin).

Found %: N 5.08, 5.00

$C_{13}H_{15}Cl_2ON$. Calculated %: N 5.14

7,7-Dichloro-6-heptenylamine

1,1,7-Trichloro-1-heptene (12 g) was heated with 8 g of ammonia in 60 ml of methanol at 80-85° for eight hours. The residue after removal of methanol and ammonia was treated in the same way as in the case of 5,5-dichloro-4-pentenylamine. Vacuum distillation yielded 6.1 g (56.2%) of 7,7-dichloro-6-heptenylamine, b.p. 102-103° (7 mm); n_D^{20} 1.4842; d_4^{20} 1.1039; Found MR 47.19; Calculated MR 47.21.

Found %: N 7.52, 7.52

$C_7H_{13}Cl_2N$. Calculated %: N 7.69

The benzoyl derivative melted at 37.5-38° (from ligroin).

Found %: N 4.72, 4.97

$C_{14}H_{17}Cl_2NO$. Calculated %: N 4.89

9,9-Dichloro-8-nonenylamine

A solution of 23 g of 1,1,9-trichloro-1-nonene in 150 ml of methanol containing 15 g of ammonia was heated at 80-85° for ten hours. After removal of ammonia and methanol, the residue was treated in the same way as in the case of 5,5-dichloro-4-pentenylamine. Vacuum distillation yielded 10.6 g (50.5%) of the dichlorononenylamine, b.p. 100-101° (3 mm); n_D^{20} 1.4822; d_4^{20} 1.0599; Found MR 56.50; Calculated MR 56.45.

Found %: N 6.60, 6.75

$C_9H_{17}Cl_2N$. Calculated %: N 6.66

The benzoyl derivative melted at 44.5-45.5° (from ligroin).

Found %: N 4.56, 4.47

$C_{16}H_{21}Cl_2NO$. Calculated %: N 4.60

5,5,5-Trichloropentylamine

1,1,1,5-Tetrachloropentane (25 g) was heated in a steel ampoule with 20 g of ammonia and 100 ml of methanol at 85-90° for ten hours. The methanol and ammonia were driven off in a water bath. The crystalline residue was washed on the filter with chloroform, and then treated, with cooling, with a solution of caustic soda. The oil that separated was extracted with ether, and the ether extract was dried with sodium sulfate. Vacuum distillation of the product yielded 3.5 g of dichloropentenylamine and 13.2 g (58.2%) of trichloropentylamine; there was an appreciable residue in the distillation flask. The boiling point of 5,5,5-trichloropentylamine is 69-70° (1.2 mm);

n_D^{20} 1.4862; d_4^{20} 1.2619; Found MR 43.35; Calculated MR 43.21.

Found %: C 31.56, 31.60; H 5.31, 5.36; N 7.31, 7.33

$C_5H_{10}Cl_3N$. Calculated %: C 31.49; H 5.24; N 7.35

The benzoyl derivative melted at 95-96° (from aqueous alcohol).

Found %: N 4.70, 4.63

$C_{12}H_{14}Cl_3NO$. Calculated %: N 4.75

The hydrolysis of 5,5,5-trichloropentylamine with concentrated sulfuric acid yielded 5-aminovaleric acid, m.p. 155-156°. On standing 5,5,5-trichloropentylamine forms a precipitate of its hydrochloride, m.p. 229-230° (from water).

Found %: C 26.59, 26.64; H 4.98, 5.05; Cl 63.00, 62.90

$C_5H_{11}Cl_4N$. Calculated %: C 26.43; H 4.84; Cl 62.56

When the amine is heated above 130-140°, a vigorous reaction sets in with formation of hydrochloride and resins.

6,6,6-Trichlorohexanenitrile

A mixture of 63 g of 1,1,1,5-tetrachloropentane and a solution of 20 g of sodium cyanide and 3 g of sodium iodide in 150 ml of ethanol was heated with stirring for 10-12 hours. The alcohol was driven off in a water bath, and water was added to the residue to dissolve salts. The oil that was present was extracted with carbon tetrachloride, and the solution formed was dried with calcium chloride. Vacuum distillation yielded 8 g of the original tetrachloropentane and 48 g (80%) of 6,6,6-trichlorohexanenitrile, b.p. 91-92° (1.5 mm); n_D^{20} 1.4822; d_4^{20} 1.2877; Found MR 44.41; Calculated MR 44.33.

Found %: N 6.90, 7.08

$C_6H_8Cl_3N$. Calculated %: N 6.98

6,6-Dichlorohexylamine

6,6,6-Trichlorohexanenitrile (25 g) dissolved in 60 ml of methanol was hydrogenated in presence of 5 g of Raney nickel and hydrogen at 60-80°, 100 atm, for four hours. After removal of catalyst, the methanol was distilled off in a water bath. Dilute hydrochloric acid was added to the residue, and the undissolved oil was extracted with chloroform. The hydrochloric acid solution was rendered alkaline with caustic potash solution, cooling being applied. Separation occurred of the base and also of nickel hydroxide, which had to be removed by filtration. The amine was extracted with ether, and the ether extract was dried with potassium carbonate. Vacuum distillation of the product yielded a small first fraction (about 1 g) and 8.1 g of 6,6-dichlorohexylamine, b.p. 93-94° (7 mm); n_D^{20} 1.4730; d_4^{20} 1.1088; Found MR 43.01; Calculated MR 43.06.

Found %: N 8.12, 8.18

$C_6H_{13}Cl_2N$. Calculated %: N 8.23

From the chloroform solution, 7.2 g of unchanged nitrile was recovered.

The benzoyl derivative melted at 56-57° (from ligroin).

Found %: N 5.07, 5.05

$C_{13}H_{17}Cl_2NO$. Calculated %: N 5.11

The dichlorohexylamine underwent no change on being kept for a long time.

Diethyl 5,5,5-Trichloropentylmalonate

1,1,1,5-Tetrachloropentane (52 g) was added to sodiomalonic ester prepared in 60 ml of absolute ethanol from 32 g of malonic ester and 4.6 g of sodium. The solution was heated under reflux for eight hours, and then, to the cooled solution, water was added until the separation of oil was complete. The oil was extracted with chloroform, and the chloroform solution was dried over sodium sulfate. Vacuum distillation yielded 27 g of a first fraction, b.p. 76-140° (2.5 mm) and 43.1 g of diethyl 5,5,5-trichloropentylmalonate, b.p. 141-142.5° (2.5 mm); n_D^{20} 1.4624; d_4^{20} 1.2130; Found MR 75.64; Calculated MR 75.53.

Found %: C 43.70, 43.70; H 5.69, 5.76; Cl 31.34, 31.14

$C_{12}H_{19}Cl_3O_4$. Calculated %: C 43.20; H 5.69; Cl 31.92

7,7,7-Trichloroheptanoic Acid

A mixture of 43 g of the ester prepared as described above, 80 ml of glacial acetic acid, 50 ml of concentrated hydrochloric acid, and 60 ml of water was heated under reflux for ten hours. The acetic acid was then driven off under reduced pressure, and the oil remaining was extracted with chloroform. The residue after removal of solvent was heated at 170-180° until evolution of carbon dioxide ceased (30 minutes). When it had cooled, the product was dissolved in a slight excess of 10% aqueous caustic soda. The alkaline solution was extracted with ether and then acidified with hydrochloric acid. The trichloroheptanoic acid, which separated as an oil, was extracted with chloroform. Vacuum distillation yielded 22.5 g (73.5%) of 7,7,7-trichloroheptanoic acid, b.p. 120-121° (0.5 mm), m.p. 36-37° (from petroleum ether).

Found %: Cl 45.51, 45.48
$C_7H_{11}Cl_3O_2$. Calculated %: Cl 45.61

Hydrolysis of 7,7,7-trichloroheptanoic acid with concentrated hydrochloric acid gave a 92% yield of pimelic acid (m.p. 102-103°). The acid chloride of 7,7,7-trichloroheptanoic acid (b.p. 91-92°/1 mm) was obtained in almost quantitative yield by the action of thionyl chloride. The amide was prepared by the action of the acid chloride on aqueous ammonia, with cooling; m.p. 78-79°.

Found %: N 5.95, 6.04
$C_7H_{12}Cl_3ON$. Calculated %: N 6.02

6,6,6-Trichlorohexylamine

Concentrated sulfuric acid (40 ml) was added over a period of one hour at 40-45° to a solution of 20 g of 7,7,7-trichloroheptanoic acid in 60 ml of benzene containing 4.5 g of hydrazoic acid. The required temperature was maintained by means of external cooling. After the addition of the sulfuric acid the mixture was stirred for three hours further at the same temperature (until bubbles of gas ceased to separate). At the same time some hydrolysis of the trichloromethyl group was brought about by the sulfuric acid; it was for this reason that the temperature was not allowed to rise above 45°. When reaction was complete, the mixture was cooled and poured into ice water. The benzene layer was separated, and the sulfuric acid solution was carefully made alkaline (with cooling) by means of caustic soda solution. The oil that separated was extracted with ether, and the ether solution was dried with sodium sulfate. Vacuum distillation yielded 5.1 g (34.5%) of 6,6,6-trichlorohexylamine, b.p. 78-79° (1.2 mm); n_D^{20} 1.4843; d_4^{20} 1.2192; Found MR 48.01; Calculated MR 47.93.

Found %: N 6.85, 6.98
$C_6H_{12}Cl_3N$. Calculated %: N 6.84

The benzoyl derivative melted at 70.5-71.5°.

Found %: N 4.75, 4.60
$C_{13}H_{16}Cl_3NO$. Calculated %: N 4.53

7,7,7-Trichloroheptylamine

A solution of 30.5 g of 1,1,1,7-tetrachloroheptane in 150 ml of methanol containing 16 g of ammonia was heated in a steel ampoule at 85-90° for eight hours. The methanol and ammonia were driven off in a water bath, and the residue was treated as in the case of 5,5-dichloro-4-pentenylamine. Vacuum distillation of the product yielded 6.4 g of 7,7-dichloro-6-heptenylamine, b.p. 78-80° (1.5 mm) and 8.3 g (29.7%) of 7,7,7-trichloroheptylamine, b.p. 95-96° (1.5 mm). A considerable residue remained in the distillation flask, and this, on being heated, decomposed with evolution of hydrogen chloride. The trichloroheptylamine had n_D^{20} 1.4828; d_4^{20} 1.1857; Found MR 52.67; Calculated MR 52.55.

Found %: C 38.22, 38.40; H 6.48, 6.44; N 6.45
$C_7H_{14}Cl_3N$. Calculated %: C 38.44; H 6.40; N 6.40

The benzoyl derivative melted at 91-92° (from aqueous alcohol).

Found %: N 4.30, 4.45
$C_{14}H_{18}Cl_3NO$. Calculated %: N 4.34

SUMMARY

1. By the reaction of tetrachloroalkanes and trichloroalkenes having the structures $CCl_3(CH_2)_nCl$ and $CCl_2=CH(CH_2)_nCl$ with ammonia, the following amines have been prepared: $CCl_3(CH_2)_4NH_2$, $CCl_3(CH_2)_6NH_2$, $CCl_2=CH(CH_2)_3NH_2$, $CCl_2=CH(CH_2)_5 \cdot NH_2$, $CCl_2=CH(CH_2)_7NH_2$, and their benzoyl derivatives.

2. Hydrogenation of polychloro nitriles of structure $CCl_3(CH_2)_4CN$ and $CCl_2=CH(CH_2)_4CN$ by means of hydrogen under pressure in presence of Raney nickel has yielded amines of structure: $CHCl_2(CH_2)_4NH_2$ and $CCl_2=CH(CH_2)_3NH_2$ and their benzoyl derivatives.

3. 6,6,6-Trichlorohexylamine has been prepared by the action of hydrazoic acid on 7,7,7-trichloroheptanoic acid. The trichloroheptanoic acid was prepared from 1,1,1,5-tetrachloropentane by the malonic ester synthesis. The acid chloride and amide of 7,7,7-trichloroheptanoic acid have been prepared.

Received January 24, 1953.

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METHODS FOR THE PREPARATION OF MIXED ALKYL ORTHOTITANATES HAVING THE STRUCTURES $(RO)_3TiOR'$ and $(RO)_2Ti(OR')_2$

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Among the organic compounds containing titanium, no compounds are known in which alkoxyl groups of more than one kind are present. Such compounds, however, are undoubtedly of interest from the point of view of reactivity and of their application for purposes of synthesis, particularly for the synthesis of titanoxane compounds. We considered that, of the possible methods of synthesis of mixed alkyl orthotitanates, the most promising were (a) the complete alkoxylation of alkoxyhalotitaniums of the type $(RO)_nTiX_{4-n}$, where n = 1, 2, 3, and (b) the action of titanium tetrachloride on a mixture of alcohols in presence of substances that will bind hydrogen chloride.

In titanium chemistry alcoholysis of the bond Ti – Cl is effected by the action of sodium alkoxides or of alcohols in presence of ammonia and amines. Having regard to our experience in working with alkyl orthotitanates, we decided to effect the synthesis of mixed alkyl orthotitanates by the action of alcohols on alkoxyhalotitaniums in presence of ammonia and amines in accordance with the equation:

$$(RO)_nTiX_{4-n} + (4-n)R'OH + R''_3N \longrightarrow (RO)_nTi(OR')_{4-n} + R''_3N \cdot HX.$$

The alkoxyhalotitaniums accessible at present are trialkoxychlorotitaniums [1] and alkoxytrichlorotitaniums [2]. With regard to dialkoxydichlorotitaniums, these are readily accessible only in the form of double compounds with alcohols [3, 4]. Their preparation free from alcohols presents some difficulties, and their use as starting materials for the synthesis of mixed esters of orthotitanic acid is therefore inconvenient.

The second method for the synthesis of mixed alkyl orthotitanates, which consists in the direct action of titanium tetrachloride on a mixture of alcohols in presence of ammonia and an amine is the simplest and most convenient, since it yields these compounds in one stage from very accessible starting substances. It is probable, however, that in the application of this method, a mixture of products will be obtained in a number of cases.

Study of the chemical properties of alkyl orthotitanates has shown that in the lower members the alkoxy groups are very mobile. They are, for example, very readily eliminated by the action of chlorine and bromine [4], and also, in a number of cases, by the action of pyridine hydrochloride [5]. The ready hydrolysis of alkyl orthotitanates points in the same direction [6]. It was to be expected, therefore, that it would be necessary to prepare mixed esters of orthotitanic acid under mild conditions in order to avoid their disproportionation, leading to the formation of a mixture of products, e. g. as follows:

$$4(RO)_3TiOR' \xrightarrow[\text{heat}]{} 3(RO)_4Ti + (R'O)_4Ti.$$

In view of these considerations we carried out the synthesis of mixed alkyl orthotitanates in the cold, distilled off the solvent at a pressure of 25-40 mm, and distilled off the esters at 1-2 mm, distilling only a small amount at a time.

We have studied the action of isopentyl alcohol on chlorotriethoxytitanium, of ethyl and isopentyl alcohols on chlorotripropoxytitanium, of ethyl, propyl, isopropyl, and allyl alcohols on chlorotriisopentyloxytitanium, of isopentyl alcohol on trichloro(2-methoxyethoxy)titanium, of hexyl alcohol on trichloroisobutoxytitanium, of isopropyl alcohol on trichloro(2-ethoxyethoxy)titanium, and of ethyl alcohol on trichloroisopentyloxytitanium. In some of the reactions ammonia was used to bind the hydrogen chloride, and in others pyridine and ammonia were

introduced successively into the reaction mixture [7]. In reactions performed in presence of ammonia and without addition of pyridine to the reaction mixture, it was not found possible to obtain completely pure mixed esters of orthotitanic acid. Analysis of the products gave carbon contents that were too high (by about 1%).

When the reactions were carried out in presence of pyridine with subsequent addition of ammonia, a number of mixed alkyl orthotitanates were obtained in the pure state. Thus, under these conditions it was found possible to effect the smooth, complete alkoxylation of alkoxychlorotitaniums by the action of primary alcohols (ethyl, propyl), secondary alcohols (isopropyl), primary alcohols having a branched chain (isopentyl), and unsaturated alcohols (allyl); the following esters were obtained: ethyl triisopentyl, triisopentyl isopropyl, isopentyl tripropyl, and allyl triisopentyl orthotitanates. All these substances are rather viscous, hygroscopic, readily hydrolyzable, colorless liquids, which can be vacuum-distilled. It must be pointed out that the thermal stability of the mixed alkyl orthotitanates varies greatly according to the nature of the alkoxyl groups present. Some of the substances obtained withstood two vacuum distillations, whereas others, already in the second distillation, boiled over a range of 15-20°.

In a number of cases we succeeded in obtaining mixed alkyl orthotitanates by the direct action of titanium tetrachloride on a mixture of alcohols in presence of pyridine and ammonia. In its general form, this reaction may be expressed as follows:

$$nROH + (4-n)R'OH + TiCl_4 + 4R''_3N \longrightarrow (RO)_nTi(OR')_{4-n} + 4R''_3N \cdot HCl.$$

When allyl and isopentyl alcohols were taken in a molar ratio of 1:3, allyl triisopentyl orthotitanate was obtained. When the alcohols were taken in equimolecular proportions, the reaction product was diallyl diisopentyl orthotitanate. Finally, when allyl and isopentyl alcohols were taken in the ratio 3:1, triallyl isopentyl orthotitanate was obtained. In each case the ester named was the sole reaction product.

It must be pointed out that the course of the reaction of a mixture of alcohols with titanium tetrachloride depends on the nature of the alcohols taken. Thus, by the action of titanium tetrachloride on an equimolecular mixture of isopentyl and propyl alcohols we obtained a 33% yield of isopentyl tripropyl orthotitanate, but no diisopentyl dipropyl orthotitanate.

The mixed alkyl orthotitanates prepared by this method were also viscous, hygroscopic, readily hydrolyzable liquids, which could be vacuum-distilled. The isopentyl tripropyl orthotitanate obtained by this method was found to be identical in all its properties with the substance obtained by the action of isopentyl alcohol on chlorotripropoxytitanium. In the same way the substances obtained by the action of allyl alcohol on chlorotriisopentyloxytitanium and by the action of titanium tetrachloride on a mixture of the corresponding alcohols were found to be identical.

EXPERIMENTAL

All of the experiments described below were carried out with carefully dried reactants under conditions that prevented access of atmospheric moisture to the apparatus.

Preparation of Mixed Alkyl Orthotitanates by the Action of Alcohols on Alkoxychlorotitaniums

Preparation of Triisopentyl Isopropyl Orthotitanate $i\text{-}C_3H_7OTi[OCH_2CH_2CH(CH_3)_2]_3$

A solution of 11.60 g (0.03 mole) of chlorotriisopentyloxytitanium in 60 ml of benzene was added slowly from a dropping funnel to a stirred, cooled (ice water) mixture of 2.00 g (0.03 mole) of isopropyl alcohol, 2.70 g (0.03 mole) of pyridine, and 60 ml of benzene contained in a three-necked flask fitted with mercury-sealed stirrer, dropping funnel, and reflux condenser. Ammonia was then passed into the flask for two hours. The precipitated pyridine hydrochloride and ammonium chloride were filtered off, and benzene and unchanged pyridine were distilled off at 25-30 mm. The triisopentyl isopropyl orthotitanate formed in the reaction was distilled off under reduced pressure; it came over at 154-155° (1.5 mm); n_D^{20} 1.4870; yield 65%.

	Found %:	C 58.60, 58.70;	H 10.93, 11.19;	Ti 13.00, 13.10
$C_3H_7OTi(OC_5H_{11})_3$.	Calculated %:	C 58.68;	H 10.94;	Ti 13.00

Preparation of Ethyl Triisopentyl Orthotitanate $C_2H_5OTi(OC_5H_{11}\text{-}i)_3$

The procedure of the previous experiment was followed, the substances taken for reaction being 2.00 g (0.043 mole) of ethyl alcohol, 3.40 g (0.043 mole) of pyridine, and 15.00 g (0.043 mole) of chlorotriisopentyloxytitanium. Ammonia was passed into the reaction mixture for two hours. The substance obtained after removal of benzene and unchanged pyridine distilled at 151-153° (2 mm); n_D^{20} 1.4910; yield of crude product 85%.

	Found %:	C 57.87, 58.14;	H 11.06, 10.87;	Ti 13.52, 13.54
$C_2H_5OTi(OC_5H_{11})_3$.	Calculated %:	C 57.61;	H 10.80;	Ti 13.51

Preparation of Allyl Triisopentyl Orthotitanate $CH_2 = CH - CH_2OTi(OC_5H_{11}\text{-}i)_3$

The same procedure was followed, the substances taken for reaction being 2.50 g (0.043 mole) of allyl alcohol, 3.40 g (0.043 mole) of pyridine, and 15.0 g (0.043 mole) of chlorotriisopentyloxytitanium. Ammonia was passed into the reaction mixture for two hours. The substance obtained distilled at 162.5-163.5° (1.5 mm); n_D^{20} 1.4960; yield of crude product 82%.

	Found %:	C 59.16, 58.85;	H 10.65, 10.50;	Ti 13.19, 13.07
$C_3H_5OTi(OC_5H_{11})_3$	Calculated %:	C 59.00;	H 10.45;	Ti 13.07

Preparation of Isopentyl Tripropyl Orthotitanate $(n\text{-}C_3H_7O)_3TiOC_5H_{11}\text{-}i$

The same procedure was followed, the substances taken for reaction being 4.06 g (0.046 mole) of isopentyl alcohol, 3.6 g (0.046 mole) of pyridine, and 12 g (0.046 mole) of chlorotripropoxytitanium. Ammonia was passed into the reaction mixture for two hours. The substance obtained distilled at 127-130° (1 mm); n_D^{20} 1.4950; yield 88%.

	Found %:	C 53.67, 53.92;	H 10.38, 10.50;	Ti 15.68, 15.74
$(C_3H_7O)_3TiOC_5H_{11}$	Calculated %:	C 53.84;	H 10.33;	Ti 15.33

Preparation of Triisopentyl Propyl Orthotitanate $n\text{-}C_3H_7OTi(OC_5H_{11}\text{-}i)_3$

The same procedure was followed, the substances taken for reaction being 2.10 g (0.034 mole) of propyl alcohol, 2.76 g (0.034 mole) of pyridine, and 12.26 g (0.035 mole) of chlorotriisopentyloxytitanium. Ammonia was passed into the reaction mixture for two hours. The substance obtained distilled at 149.5-151° (1.5-2 mm); n_D^{20} 1.4893; yield of crude product 98%.

	Found %:	C 59.11, 59.17;	H 11.04, 10.87;	Ti 12.89, 12.83
$C_3H_7OTi(OC_5H_{11})_3$.	Calculated %:	C 58.68;	H 10.94;	Ti 13.00

Preparation of Mixed Alkyl Orthotitanates by the Action of Titanium Tetrachloride on a Mixture of Alcohols

Preparation of Allyl Triisopentyl Orthotitanate $(i\text{-}C_5H_{11}O)_3TiOCH_2 - CH = CH_2$

A solution of 21.5 g (0.113 mole) of titanium tetrachloride in 60 ml of benzene was added slowly to a stirred and cooled (ice water) mixture of 30 g (0.340 mole) of isopentyl alcohol, 6.6 g (0.113 mole) of allyl alcohol, 35.9 g (0.45 mole) of pyridine, and 60 ml of benzene contained in a three-necked flask fitted with mercury-sealed stirrer, dropping funnel, and reflux condenser. When the whole of the titanium tetrachloride had been added, ammonia was passed for two hours. Precipitated pyridine hydrochloride and ammonium chloride were filtered off, and benzene and unchanged pyridine were distilled off at 25-35 mm. The residual viscous liquid all distilled over at 149-149.5° (0.5 mm). In a second distillation the substance distilled at 157.5-158° (1 mm); n_D^{20} 1.4960; yield of crude product 27.5 g (66%).

	Found %:	C 58.95, 58.94;	H 10.60, 10.50;	Ti 13.15, 13.24
$C_3H_5OTi(OC_5H_{11})_3$.	Calculated %:	C 59.00;	H 10.45;	Ti 13.07

Hence, in this experiment, the sole titanium-containing product obtained was allyl triisopentyl orthotitanate, identical in all its properties with the substance obtained by the action of allyl alcohol on chlorotripentyloxytitanium, as described above.

Preparation of Diallyl Diisopentyl Orthotitanate $(CH_2 = CH - CH_2O)_2Ti(OC_5H_{11}\text{-}i)_2$

The procedure of the preceding experiment was followed, the substances taken for reaction being 13.2 g (0.22 mole) of allyl alcohol, 20.0 g (0.22 mole) of isopentyl alcohol, 35.9 g (0.11 mole) of pyridine, and 21.6 g (0.11 mole) of titanium tetrachloride. Ammonia was passed into the reaction mixture for two hours. The diallyl diisopentyl orthotitanate obtained distilled at 160-161.5° (1 mm); n_D^{20} 1.5050; yield of crude product 77%.

	Found %:	C 57.41, 57.15;	H 9.58, 9.86;	Ti 14.49, 14.35
$(C_3H_5O)_2Ti(OC_5H_{11})_2$.	Calculated %:	C 57.14;	H 9.59;	Ti 14.24

Preparation of Triallyl Isopentyl Orthotitanate $(CH_2 = CH - CH_2O)_3TiOC_5H_{11}\text{-}i$

The same procedure was followed, the substances taken for reaction being 19.8 g (0.34 mole) of allyl alcohol, 10.0 g (0.11 mole) of isopentyl alcohol, 35.9 g (0.45 mole) of pyridine, and 21.6 g (0.11 mole) of titanium

tetrachloride. Ammonia was passed into the reaction mixture for two hours. The triallyl isopentyl orthotitanate obtained distilled at 150-151° (1 mm); n_D^{20} 1.5222, yield of crude product 27 g (77.5%).

	Found %:	C 54.45, 54.30; H 8.71, 8.68; Ti 15.74, 15.71
$(C_3H_5O)_3TiOC_5H_{11}$.	Calculated %:	C 54.90; H 8.56; Ti 15.64

In a second distillation the substance distilled over a wide range, 151-165° (1 mm), evidently owing to disproportionation of triallyl isopentyl orthotitanate, effected by heat.

Preparation of Isopentyl Tripropyl Orthotitanate $(n\text{-}C_3H_7O)_3TiOC_5H_{11}\text{-}i$

The same procedure was followed, the substances taken for reaction being 10.5 g (0.17 mole) of propyl alcohol, 15.5 g (0.17 mole) of isopentyl alcohol, 27.8 g (0.35 mole) of pyridine, and 16.7 g (0.088 mole) of titanium tetrachloride. Ammonia was passed into the reaction mixture for two hours. After removal of benzene and unchanged pyridine there remained 26.9 g of a viscous liquid, which corresponded to almost quantitative utilization of the mixture of alcohols taken. This liquid distilled over the range 152.5-164° (2 mm), and from the lower fraction in a second distillation a product b.p. 128-130° (1 mm) and n_D^{20} 1.4940, was isolated; it was identical in all of its properties with the isopentyl tripropyl orthotitanate obtained by the action of isopentyl alcohol on chlorotripropoxytitanium (see above). Analysis confirmed that the product had this composition.

	Found %:	C 54.25, 54.10; H 10.40, 10.48; Ti 14.80, 14.89
$(C_3H_7O)_3TiOC_5H_{11}$.	Calculated %:	C 53.84; H 10.33; Ti 15.33

The yield of pure isopentyl tripropyl orthotitanate was 33%, based on the amount of propyl alcohol taken. The higher-boiling fractions of the mixture of products obtained were not investigated further.

Disproportionation of Isopentyl Tripropyl Orthotitanate when Heated

Pure isopentyl tripropyl orthotitanate (5 g) from the preceding experiment was distilled under more severe conditions (6 mm). During distillation the substance underwent disproportionation, as evidenced by the fact that it distilled over the range 154-174°.

SUMMARY

1. A method for the synthesis of mixed alkyl orthotitanates has been developed: it consists in the action of alcohols on alkoxychlorotitaniums in presence of pyridine and ammonia.

2. Another method for the synthesis of mixed alkyl orthotitanates has been developed: it consists in the action of titanium tetrachloride on a mixture of alcohols in presence of pyridine and ammonia.

3. Members of a previously undescribed class of compounds have been prepared: triisopentyl isopropyl orthotitanate, ethyl isopentyl orthotitanate, allyl triisopentyl orthotitanate, triisopentyl propyl orthotitanate, isopentyl tripropyl orthotitanate, triallyl isopentyl orthotitanate, and diallyl diisopentyl orthotitanate.

When this paper was already prepared for publication, an article [8] appeared in which the preparation of some dialkyl diaryl orthotitanates by the partial transesterification of tetrabutyl orthotitanate is described. The products described, however, were not purified in any way, and the analytical results given for titanium are in good agreement also with an equimolecular mixture of the corresponding symmetrical alkyl orthotitanates. In the same paper the author refers to his preparation of 2-chloroethyl orthotitanate and benzyl orthotitanate, substances already described by us in 1951 [4].

Received March 27, 1953.

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* See Consultants Bureau Translation, page 81

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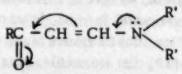
COMMUNICATION 2. SOME REACTIONS OF ALKYL 2-DIALKYLAMINOVINYL KETONES

N. K. Kochetkov

In the previous communication [1], which was concerned with the synthesis of alkyl 2-dialkylaminovinyl ketones, we suggested, on the basis of an examination of the physical properties of these compounds, that their molecules possess high polarization:



Such polarization, of course, should be reflected in the chemical properties of alkyl 2-dialkylaminovinyl ketones, and some of these properties are examined in this paper.

In accord with the above scheme, which indicates an electronic displacement from the nitrogen to the carbonyl group, it may be expected that, in comparison with their saturated analogs, the Mannich bases, alkyl 2-dialkylaminovinyl ketones will show suppression of basic properties and reduced activity, both at the double bond and at the carbonyl group. The question of the reduction in basic properties has already been considered by us [1]. In order to decide the question of the activity of the double bond, we have studied the catalytic hydrogenation of these compounds.

The question of the hydrogenation of vinylogs of amides, to which class alkyl 2-dialkylaminovinyl ketones belong, cannot be regarded as settled. The results of one group of investigators [2] indicate that vinologs of amides (more complex in structure than the compounds that we have prepared) do not undergo normal hydrogenation, but suffer hydrogenolysis at the C – N bond. On the other hand, the results of other authors indicate that 1-dimethylamino-1,4-hexadien-3-one $CH_3CH = CHCOCH = CHN(CH_3)_2$ undergoes normal hydrogenation at both double bonds.

Our experiments on the hydrogenation of alkyl 2-dialkylaminovinyl ketones have shown that these compounds absorb hydrogen with great difficulty. Thus, when palladium on carriers (charcoal, barium carbonate) is used, hydrogenation stops completely when about 0.05 of a molecular proportion of hydrogen has been absorbed. When platinum oxide is used, hydrogenation again goes very slowly: in the course of 10-15 hours one molecule of hydrogen is absorbed, and in all cases about half of the original alkyl 2-dialkylaminovinyl ketone remains in the reaction mixture and, owing to hydrogenolysis of the C – N bond, a saturated ketone is formed. We have made a detailed investigation of the hydrogenation of 4-diethylamino-3-buten-2-one in presence of platinum. From the reaction mixture we isolated some of the original substance, and we showed that 2-butanone, identified as the dinitrophenylhydrazone, and diethylamine, isolated as the picrate, were formed. None of the normal reaction product (4-diethylamino-2-butanone) was formed. It may be concluded from this behavior that the primary reaction during hydrogenation leads to cleavage of the C – N bond, and the 3-buten-2-one formed is hydrogenated at the double bond:

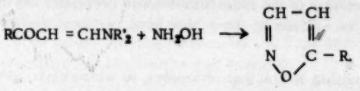
$$CH_3COCH = CHN(C_2H_5)_2 \xrightarrow[(Pt)]{H} NH(C_2H_5)_2 + CH_3COCH = CH_2 \longrightarrow CH_3COC_2H_5.$$

The other possibility – first hydrogenation of the double bond, and then hydrogenolysis – must be excluded, since it is well known that Mannich bases form amino alcohols when hydrogenated, and do not undergo hydrogenolysis at the C – N bond [4].

Our experiments, therefore, confirm the results concerning the hydrogenolysis of vinologs of amides and raise doubts concerning the results of British authors, which indicate that alkyl 2-aminovinyl ketones undergo normal hydrogenation [3]. Our results indicate not only the lability of the C – N bond, but also the strong suppression of the double bond in alkyl 2-dialkylaminovinyl ketones.

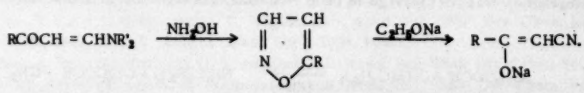
A second fact that demonstrates particularly clearly the deactivation of the double bond is the complete loss of dienophilic activity in aminovinyl ketones. As is well known, α,β-unsaturated ketones are among the most active dienophiles. 3-Buten-2-one, for example, reacts very vigorously with cyclopentadiene [5]. Alkyl 2-chlorovinyl ketones, though not reacting so vigorously, are still very active dienophiles [6, 7], and they condense to the extent of 70-85% with cyclopentadiene at room temperature. On the contrary, 4-dimethylamino-3-buten-2-one does not react with cyclopentadiene, one of the most active dienes, even when heated for many hours at 180°: it may all be recovered unchanged.

In order to clarify the question of the activity of the carbonyl group in alkyl 2-dialkylaminovinyl ketones, it was of interest to study their reaction with nitrogenous bases. It might be supposed [8] that, owing to the mobility of the dialkylamino group, the reaction would go in a way similar to that already found by us for alkyl 2-chlorovinyl ketones [9, 10], i.e., would be accompanied by cyclization and formation of the corresponding heterocycle. We selected the reaction of alkyl 2-dialkylaminovinyl ketones with hydroxylamine for detailed investigation. It was found that, when alkyl 2-dialkylaminovinyl ketones were heated with hydroxylamine in methanol for 5-6 hours, alkylisoxazoles were formed smoothly in 65-85% yield, so that in this respect dialkylaminovinyl ketones react like 2-chlorovinyl ketones. Investigation of the alkylisoxazoles formed, however, showed that there is an essential difference between these reactions. When alkyl 2-chlorovinyl ketones react with hydroxylamine hydrochloride, then as Kochetkov, Nesmeyanov, and Semenov showed [10], the isoxazoles obtained consist of a mixture of 3- and 5-alkyl compounds (γ - and α-isomers), in which there is 60% of 5-alkylisoxazole. Treatment of the alkylisoxazoles obtained from alkyl 2-dialkylaminovinyl ketones with sodium alkoxide, following Claisen [11], gave the sodium salt of the corresponding β-keto nitrile in more than 90% yield. This indicates that the isoxazoles formed consist mainly of 5-alkylisoxazole (α-isomer), and it is possible, considering the imperfections of the Claisen method from the analytical point of view, that pure α-isomer is actually obtained. The dominant direction of the reaction between aminovinyl ketones and hydroxylamine may therefore be expressed by the equation



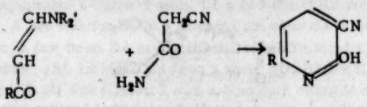
This result indicates quite definitely that the first step in the reaction is the replacement of the dialkylamino group by a hydroxylamine residue, after which cyclization occurs. It will be seen from this that the functions of the carbonyl group in 2-aminovinyl ketones, unlike those of the carbonyl group of 2-chlorovinyl ketones (which give about 40% of γ-isomer, formed by primary reaction of hydroxylamine at the carbonyl), are largely suppressed, so that it does not exhibit its typical reactivity toward a nucleophilic reagent, such as hydroxylamine. This is quite understandable from the point of view of the hypothesis advanced above concerning the great electronic displacement in the molecule of an aminovinyl ketone, leading to a reduction of the positive charge on the carbonyl carbon.

The condensation of alkyl 2-dialkylaminovinyl ketones with hydroxylamine is of importance also from the preparative point of view. By the aid of this reaction pure, or almost pure, 5-alkylisoxazoles can be prepared, and these have previously been difficultly accessible. The cleavage of 5-alkylisoxazoles by means of sodium alkoxide has an interest of its own, since by this means, from aminovinyl ketones via isoxazoles, very difficultly accessible β-keto nitriles can be obtained with an overall yield of 60-65%:



The possibilities for the utilization of 2-aminovinyl ketones for the synthesis of heterocyclic compounds are not confined to the preparation of isoxazoles. We have previously described the synthesis of 6-alkyl-2-hydroxynicotinonitriles by the condensation of acetals of β-keto aldehydes with 2-cyanoacetamide in presence of piperidine acetate [12]. We then suggested that this reaction goes through the intermediate formation of 2-(1-piperidyl)aminovinyl ketones. With the object of verifying this supposition, we have studied the reaction of alkyl

2-dialkylaminovinyl ketones with 2-cyanoacetamide, and we have found that this reaction proceeds very smoothly when a mixture of the reactants is heated in aqueous solution, the product being a 6-alkyl-2-hydroxynicotinonitrile:



This reaction is appreciably more rapid than the condensation of acetals of β-keto aldehydes with 2-cyanoacetamide, and, what is more important, it does not require the use of a condensing agent. This is a strong argument in favor of our views on the mechanism of the reaction of acetals of β-keto aldehydes with 2-cyanoacetamide [12], and we are inclined to the opinion that the condensations of 2-hydroxyvinyl ketones [14] and β-diketones [13] with 2-cyanoacetamide in presence of pyridine also go according to a similar scheme, i.e., via the intermediate formation of a 2-(1-piperidyl)aminovinyl ketone.

From the preparative point of view, the modified synthesis of substituted 2-hydroxypyridines described in this paper must be preferred to our previously developed synthesis via acetals of β-keto aldehydes, for reaction with 2-aminovinyl ketones is more rapid; also, the latter substances are more convenient to work with and can be prepared in better yields than acetals of β-keto aldehydes. The variant of the synthesis that we now propose is rendered simpler also by the fact that it is not necessary to isolate the 2-aminovinyl ketone from the reaction mixture: the aqueous solution obtained by the condensation of an alkyl 2-chlorovinyl ketone with a secondary amine, which contains the 2-aminovinyl ketone and a small excess of amine, is heated with 2-cyanoacetamide, and the hydroxynicotinonitrile separates rapidly in a yield that does not differ appreciably from that obtained when working by the original method [12]. In this form, the synthesis of 2-hydroxypyridines, which is essentially based directly on alkyl 2-chlorovinyl ketones, is the most convenient of the known methods for the synthesis of these compounds.

We have also investigated the reaction of alkyl 2-dialkylaminovinyl ketones with the Grignard reagent. 4-Dimethylamino- or 4-diethylamino-3-buten-2-one was treated with methylmagnesium iodide under the usual conditions, and after hydrolysis of the reaction mixture, 3-penten-2-one was isolated in about 20% yield and identified in the form of the dinitrophenylhydrazone:

$$CH_3COCH{=}CHN(CH_3)_2 + CH_3MgI \rightarrow CH_3COCH{=}CHCH_3.$$

This result is deserving of attention, particularly in view of the fact that simple alkyl 2-chlorovinyl ketones are known to react with organomagnesium compounds in the usual way, forming 2-chlorovinylcarbinols [15]. We again appear to have an example of the relative inactivity of the carbonyl group of a 2-dialkylaminovinyl ketone toward a nucleophilic reagent, in consequence of which the attack is directed to the β-carbon atom. The question of whether the reaction goes by 1,4-addition of the organomagnesium compound or by direct replacement of the dialkylamino group requires special investigation. We are inclined to the second supposition, because the formation of 3-penten-2-one can be established in the reaction mixture before it is hydrolyzed.

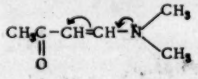
It was considered also that an investigation of the reaction of 2-dialkylaminovinyl ketones with alkyl halides would be of interest. In this case, owing to the conjugation of the electron pair of the nitrogen atom with the double bond, transfer of the reaction center could be expected; such transfer, according to Nesmeyanov's results [16], plays a decisive part in the reactions of systems of this sort. We have as yet investigated only one example of this reaction.

When 4-dimethylamino-3-buten-2-one was heated with excess of methyl iodide, a crystalline substance was quickly precipitated from the reaction mixture; it was readily soluble in water and contained halide ions: in analysis it corresponded to an addition product from one molecule of methyl iodide and one mole of the aminovinyl ketone. This compound was hydrolyzed with boiling water, and 4-hydroxy-3-methyl-3-buten-2-one $CH_3COC(CH_3){=}CHOH$ was isolated from the reaction mixture. The overall reaction may, therefore, be represented by the equation:

$$CH_3COCH{=}CHN(CH_3)_2 + CH_3I \xrightarrow{H_2O} CH_3COC(CH_3){=}CHOH + (CH_3)_2NH \cdot HI.$$

It is more convenient to carry out this reaction without isolating the intermediate addition product: 4-dimethylamino-3-buten-2-one is heated with an excess of methyl iodide, water is added to the reaction mixture, the excess of methyl iodide is driven off by heat, and the reaction product is extracted with ether. By this means the hydroxymethylbutenone was isolated in 17.4% yield.

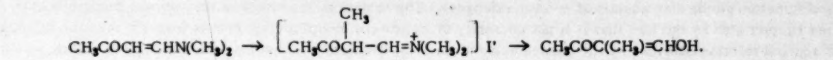
Reaction of methyl iodide with 4-dimethylamino-3-buten-2-one, therefore, proceeds with transfer of the reaction center, the nucleophilic attack being directed to the β-carbon atom:



It should be noted in this connection that dialkylaminoethyl ketones (the so-called Mannich bases) form normal alkiodides. In the saturated isologs of aminovinyl ketones, therefore, the transfer of reaction center no longer occurs. Why, in the alkylation of a dialkylaminovinyl ketone, the reaction center is not transferred to the end of the conjugated system (formation of an O-derivative) remains obscure.

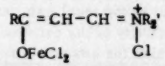
It is probable that, when methyl iodide reacts with 4-dimethylamino-3-buten-2-one, there is direct alkylation at the α-carbon atom, and not rearrangement of an initially formed methiodide. This view is supported by the fact that in the methylation of 4-diethylamino-3-buten-2-one, again only 4-hydroxy-3-methyl-3-buten-2-one is formed, and the 4-hydroxy-3-ethyl-3-buten-2-one $CH_3COC(C_2H_5)=CHOH$ that might be expected is not formed.

Our reaction can probably be represented by the following scheme:



We have found one reaction in the literature that is close in character to the one described. Robinson [17], investigating the reaction of ethyl 3-diethylaminocrotonate with methyl iodide, found that when the reaction mixture was hydrolyzed ethyl 2-methylacetoacetate was obtained. In a further study of this reaction, other authors [18], using ethyl iodide, also concluded that direct alkylation at carbon occurred.

Our investigation of the properties of alkyl 2-dialkylaminovinyl ketones has, therefore, indicated the highly peculiar nature of these compounds. It should be mentioned further that all of the compounds obtained give a color with ferric chloride. It is possible that this is to be explained by hydrolysis of the aminovinyl ketone to a β-keto aldehyde. It may be, however, that the nature of this phenomenon is more complex, for when anhydrous ferric chloride is added to a solution of an aminovinyl ketone in absolute ether, an intensely colored, ether-insoluble oil is precipitated. This indicates that the colored compound has a saltlike structure, for example



Such a hypothesis, though not yet confirmed experimentally, is in accord with the general character of alkyl 2-dialkylaminovinyl ketones.

EXPERIMENTAL

Hydrogenation of 4-Diethylamino-3-buten-2-one

4-Diethylamino-3-buten-2-one (5.0 g) was hydrogenated in alcohol (40 ml) in presence of platinum oxide (0.15 g) at room temperature. Absorption of hydrogen was very slow: 750 ml of hydrogen (calculated for one molecule 800 ml) was absorbed in 11 hours, and hydrogenation then came practically to a stop. The catalyst was filtered off, and the filtrate was distilled from a water bath, a fraction boiling up to 85° being collected. The residue was vacuum-distilled, and it all came over at 122-124° (5 mm) (2.1 g). After a second distillation the substance had b.p. 123-124° (5 mm) and n_D^{20} 1.5358, which corresponds to the constants of the original 4-diethylamino-3-buten-2-one.

The fraction of the filtrate boiling up to 85° at normal pressure was acidified with 10 ml of 10% hydrochloric acid and again distilled to dryness. The distillate was saturated with dinitrophenylhydrazine, and on the next day the crystals that had precipitated were filtered off and recrystallized from alcohol (orange-red needles, m.p. 114-115°). A mixture melting point with the dinitrophenylhydrazone of 2-butanone showed no depression.

The dry residue from the distillation was treated with 20% caustic soda and extracted with ether. The extract was washed with water, dried over magnesium sulfate, and saturated with picric acid. The precipitated crystals were filtered off and recrystallized from alcohol, yielding yellow crystals, m.p. 153-154°. A mixture melting point with diethylamine picrate showed no depression.

5-Methylisoxazole

A mixture of 14.0 g of 4-diethylamino-3-buten-2-one, 7.5 g of hydroxylamine hydrochloride, and 40 ml of methanol was heated for five hours. A hot solution of 70 g of cadmium chloride in 50 ml of water was then added to the hot reaction mixture, and after a few hours the crystals that had precipitated were filtered off, pressed dry on the filter, slightly moistened with water, and dry-distilled from a small distillation flask. The lower layer of the distillate was separated, and the upper layer was saturated with ammonium chloride and extracted with ether. The main portion of the product and the extract were united and then dried over magnesium sulfate. The ether was driven off, and the residue was distilled from a flask having a small fractionation column. The whole (4.9 g, 59%) came over at 121-122°. After redistillation the methylisoxazole had the following constants: b.p. 121-122° (750 mm); d_4^{20} 1.0224; n_D^{20} 1.4368; found MR 21.28; calculated for C_4H_5ON: MR 21.39 (nitrogen increment 2.84 [10]).

The substance (1.0686 g) was dissolved in alcohol (10 ml) and treated, under cooling, with an alcoholic solution of sodium ethoxide (1.0 g of sodium in 5 ml of alcohol), when a precipitate quickly formed. After 30 minutes 30 ml of absolute ether was added, and the precipitate was filtered off, washed with absolute ether, and dried in a vacuum. The weight of the sodium derivative of acetoacetonitrile was 1.244 g, corresponding to a content of 92% of the 5-methyl isomer. The phenylhydrazone of acetoacetonitrile was prepared by treating the sodium derivative with phenylhydrazine in aqueous medium, a little acetic acid being added. Recrystallization from alcohol yielded colorless crystals, m.p. 100-101°. The literature [19] gives m.p. 101-102° for the phenylhydrazone of acetoacetonitrile.

5-Propylisoxazole

A mixture of 13.0 g of 1-dimethylamino-1-hexen-3-one, 7.5 g of hydroxylamine hydrochloride, and 40 ml of methanol was heated for five hours, and to the mixture three times its volume of water was then added. The oil that separated was extracted with ether, the extract was dried with magnesium sulfate, the ether was driven off, and the residue was distilled from a flask having a small fractionation column. The fraction of b.p. 159-161° (9.0 g, 89%) was collected. After redistillation the propylisoxazole had the following constants: b.p. 161.0-161.5°; d_4^{20} 0.9682; n_D^{20} 1.4460; found MR 30.61; calculated for C_6H_9ON: MR 30.63; nitrogen increment 2.84 (cf. [10]).

	Found %:	N 12.54; 12.62
C_6H_9ON.	Calculated %:	N 12.60

The propylisoxazole was a colorless oil of characteristic odor.

The substance (1.0120 g) was treated with an alcoholic solution of sodium ethoxide (1 g of sodium in 15 ml of alcohol), as described for the previous experiment. The weight of precipitated sodium derivative of 3-oxohexanenitrile was 1.1214, which corresponds to a content of 91.4% of the 5-isomer. The phenylhydrazone of 3-oxohexanenitrile was prepared by the method given for the previous experiment; after crystallization from alcohol it melted at 96°.

	Found %:	N 21.03; 21.10
$C_{12}H_{15}N_3$.	Calculated %:	N 20.88

2-Hydroxy-6-methylnicotinonitrile

a) A mixture of 5.0 g of 4-dimethylamino-3-buten-2-one, 4.5 g of 2-cyanoacetamide, and 50 ml of water was heated at the boil, and after 10-15 minutes a crystalline precipitate of the condensation product began to form. After two hours at the boil, the mixture was cooled and the precipitate filtered off. The filtrate was boiled for a further two hours, and the small amount of precipitate that formed on cooling was filtered off and added to the main portion of the substance (4.1 g, 65%). Recrystallization from water yielded colorless needles, m.p. 278-280°. A mixture melting point with an authentic sample of 2-hydroxy-6-methylnicotinonitrile showed no depression. For this substance the literature gives m.p. 276-278° [12].

b) 4-Chloro-3-buten-2-one (5.0 g) was added slowly to 25 ml of a cooled, vigorously stirred 40% aqueous solution of dimethylamine. A solution of 5.0 g of 2-cyanoacetamide in 20 ml of water was then added, and the mixture was heated to the boil. After 15 minutes the condensation product began to crystallize out, and after one hour the mixture was cooled and the precipitate filtered off (3.9 g, 59%). Recrystallization from water yielded colorless needles, m.p. 279-281°.

2-Hydroxy-6-propylnicotinonitrile

A mixture of 2.1 g of 1-dimethylamino-1-hexen-3-one, 1.5 g of 2-cyanoacetamide, and 20 ml of water was heated at the boil for five hours. The mixture was cooled, and the crystalline precipitate was filtered off and washed

with cold water (1.75 g, 72%). Recrystallization from water yielded colorless needles, m.p. 147-148°. A mixture melting point with 2-hydroxy-6-propylnicotinonitrile showed no depression. For this substance the literature gives m.p. 147-148° [12], 153° [14].

2-Hydroxy-6-isobutylnicotinonitrile

This was prepared following a similar procedure from 3.5 g of 1-dimethylamino-5-methyl-1-hexen-3-one and 2.7 g of 2-cyanoacetamide. The condensation product came down as an oil, which then rapidly and completely crystallized. Recrystallization from alcohol yielded colorless needles, m.p. 148-149° (2.9 g, 74.8%). For 2-hydroxy-6-isobutylnicotinonitrile the literature [14] gives m.p. 149-150°.

Reaction of 4-Dimethylamino-3-buten-2-one with Methylmagnesium Iodide

A solution of 41.0 g of 4-dimethylamino-3-buten-2-one in an equal volume of ether was added slowly to a vigorously agitated, cooled (ice and salt) solution of methylmagnesium iodide prepared in the usual way from 47.0 g of methyl iodide and 7.0 g of magnesium in 250 ml of ether. An oil was precipitated, and this rapidly crystallized; the characteristic sharp odor of 3-penten-2-one appeared in the reaction mixture. The mixture was stirred for three hours at room temperature, and 10% hydrochloric acid was then added under cooling until the precipitate was completely dissolved. The ether layer was separated, and the aqueous layer was repeatedly extracted with ether. The extracts were dried over magnesium sulfate, and the ether was distilled off from a flask fitted with a good fractionating column. Distillation of the residue followed, a fraction boiling at 119-124° being collected. The redistilled substance had the following constants: b.p. 121-123°; d_4^{20} 0.8573; n_D^{20} 1.4390; found MR 25.81; calculated for C_5H_8O: MR 24.83. The yield was 6.9 g (19.8%). For 3-penten-2-one the literature [20] gives: b.p. 122-124°; d_4^{20} 0.8577; n_D^{20} 1.4390.

The dinitrophenylhydrazone was prepared in alcohol and recrystallized from the same solvent, yielding orange-red needles, m.p. 153-154°.

Found %: N 21.09; 21.32
$C_{11}H_{12}O_4N_4$. Calculated %: N 21.21

A mixture melting point with the dinitrophenylhydrazone of 3-penten-2-one showed no depression.

Reaction of 4-Dimethylamino-3-buten-2-one with Methyl Iodide

a) A mixture of 25.0 g of 4-dimethylamino-3-buten-2-one and 52.0 g of methyl iodide was heated at the boil for six hours. When the reaction mixture was cooled, an appreciable quantity of crystals separated. Water (50 ml) was added to the mixture, and it was again heated at the boil for 30 minutes, when the greater part of the methyl iodide was driven off with steam. The mixture was cooled and extracted with ether. The extracts were dried over sodium sulfate, the ether was driven off, and the residue was distilled. A fraction of b.p. 145-150° was collected; it solidified completely in the receiver. It was redistilled and then subjected to slow sublimation; the product (3.4 g, 17.5%) had b.p. 145-148°, m.p. 72°.

Found %: C 59.49; 59.53; H 8.18; 8.38
$C_5H_8O_2$. Calculated %: C 59.98; H 8.05

The substance, which was obtained as colorless, readily volatile crystals, was soluble in organic solvents and difficultly soluble in water. It gave a reddish-violet color with ferric chloride. For 4-hydroxy-3-methyl-3-buten-2-one the literature [21] gives b.p. 145-147°, m.p. 73°.

b) A mixture of 6.0 g of 4-dimethylamino-3-buten-2-one, 9.0 g of methyl iodide, and 30 ml of dry benzene was heated at the boil for four hours, and was then set aside for several days. The crystalline precipitate of condensation product was filtered off and recrystallized from absolute alcohol, yielding slightly colored crystals (4.5 g, 33%), m.p. 120-122° (dec.).

Found %: N 5.71; 5.62
$C_7H_{14}ONI$. Calculated %: N 5.48

The crystals were readily soluble in water, but did not dissolve in hydrocarbons. When silver nitrate was added to the aqueous solution, a precipitate of silver iodide quickly appeared. When the substance was treated with boiling water, as described above, 4-hydroxy-3-methyl-3-buten-2-one, identical with that obtained by direct hydrolysis of the reaction mixture, was isolated.

It is my pleasant duty to express my thanks to A. N. Nesmeyanov for his valuable advice and constant interest in the work.

SUMMARY

1. When alkyl 2-dialkylaminovinyl ketones are hydrogenated, hydrogenolysis of the nitrogen–carbon bond occurs, resulting in the formation of a saturated ketone and a secondary amine.

2. When alkyl 2-dialkylaminovinyl ketones react with hydroxylamine, 5-alkylisoxazoles are formed; this provides a convenient method for the synthesis of these compounds.

3. When alkyl 2-dialkylaminovinyl ketones react with 2-cyanoacetamide, 6-alkyl-2-hydroxynicotinonitriles are formed.

4. When 4-dimethylaminoamino-3-buten-2-one reacts with methylmagnesium iodide, 3-penten-2-one is formed.

5. The reaction of 4-dimethylamino-3-buten-2-one goes with transfer of reaction center, and, as a result, 4-hydroxy-3-methyl-3-buten-2-one is formed.

Received January 8, 1953

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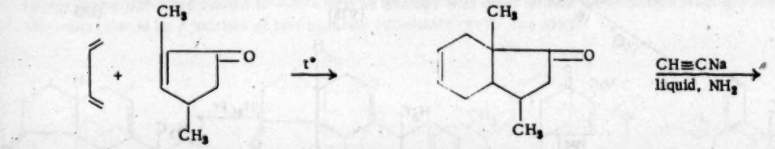
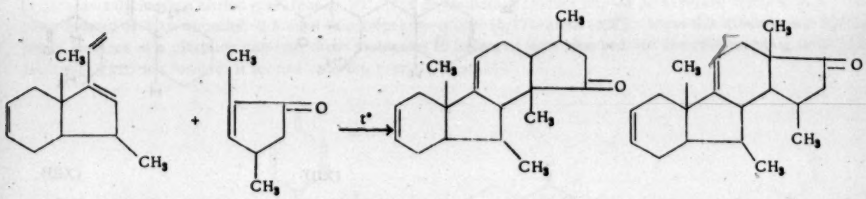
SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION XXIV. CONDENSATION OF 3a,4,7,7a-TETRAHYDRO-1,3a-DIMETHYL-3-VINYLINDENE WITH α,β-UNSATURATED CYCLIC KETONES

I. N. Nazarov and M. S. Burmistrova

In one of our previous communications [1] we described the synthesis of 3a,4,7,7a-tetrahydro-1-3a-dimethyl--3-vinylindene (I) and the diene condensation of this substance with 2,4-dimethyl-2-cyclopenten-1-one (II), which led to the preparation of the tetracyclic ketone III having a B-norcardosterane skeleton (Nazarov's nomenclature for synthetic steroids, see [2]):





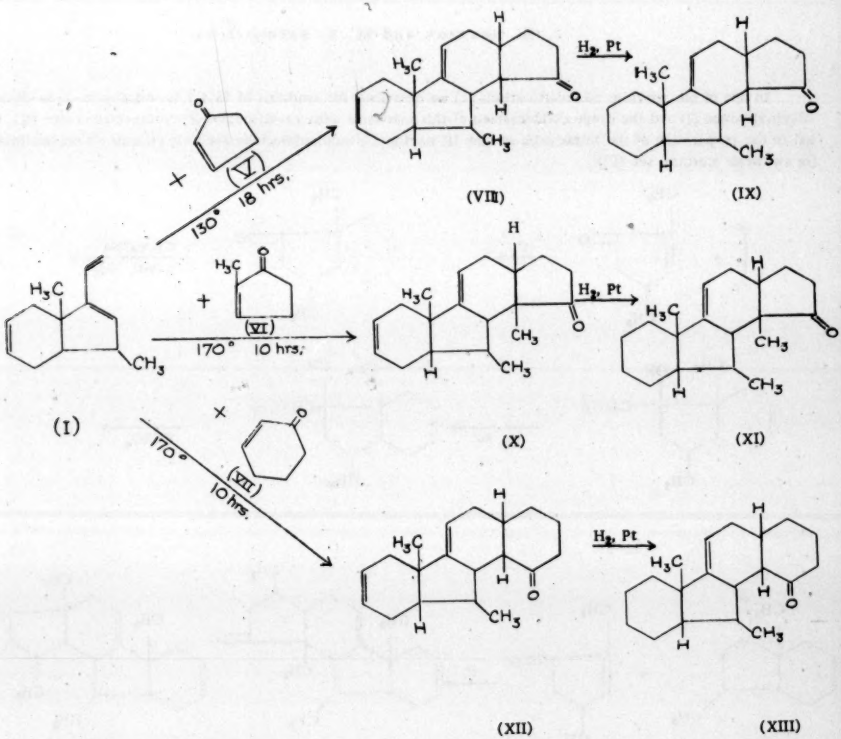
(I) (II) (III) (IV)

As we have shown in this laboratory in other cases [3], in diene condensations of α,β-unsaturated cyclic ketones with bicyclic dienes of the type 1-vinyl-Δ^1-octahydronaphthalene or 1-vinyl-Δ^1-hexahydroindene, the products always consist of mixtures of isomeric steroid ketones having the so-called "inverted" structure (having an inverted D-ring; Formula III), which differ among themselves either in spatial arrangement or in the position of the double bond formed in the diene condensation. Steroid ketones having the normal disposition of the D-ring (Formula IV) are apparently not formed in these condensations.

In the present investigation we have studied the diene condensations of 3a,4,7,7a-tetrahydro-1-3a-dimethyl-3-vinylindene (I) with 2-cyclopenten-1-one (V), 2-methyl-2-cyclopenten-1-one (VI), 2-cyclohexen-1-one (VII),

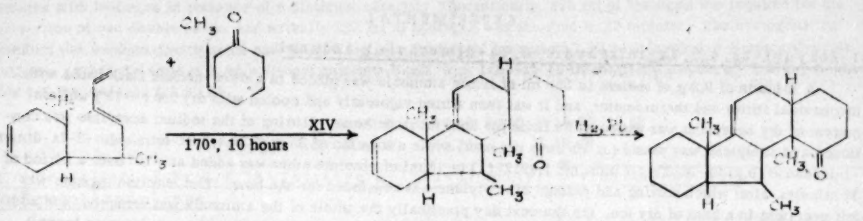
2-methyl-2-cyclohexen-1-one (XIV), and also with citraconic anhydride (XVII) and p-benzoquinone (XX). These condensations were carried out by heating the diene I at 130-170° with excess of the ketone in presence of a carbon dioxide atmosphere or of 1% of dimethylaniline in a sealed glass tube.

As a result of the condensation of the diene I with the cyclopentenone V, the methylcyclopentenone VI, and the cyclohexenone VII, yields of 30-40% were obtained of mixtures of isomers of 7,10-dimethyl-2,9-B-norcardosteradien--15-one (VIII), 7,10,14-trimethyl-2,9-B-norcardosteradien-15-one (X), and 7,10-dimethyl-2,9-B-norcardochrysadien--15-one (XII) respectively, in the form of viscous oils that did not crystallize even when strongly cooled (−35°, two hours):



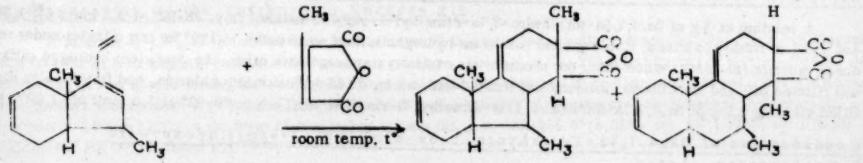
When the 2,9-diene steroid ketones VIII, X, and XII were hydrogenated in presence of a platinum catalyst, only one molecule of hydrogen was absorbed, and the corresponding Δ^9-steroid ketones IX, XI, and XIII were formed; these also were viscous noncrystallizing oils. As we have shown in other cases [3], when 2,9-diene steroid ketones are hydrogenated, only one double bond (position 2, ring A) is reduced, the double bond in the 9-position not being affected; usually, this bond is hydrogenated only with great difficulty (high temperature and pressure).

When the diene I was condensed with 2-methyl-2-cyclohexen-1-one (XIV), a viscous oil was again obtained, but this partially crystallized after long standing. Both the liquid and the crystalline solid corresponded in composition to the expected product of this diene condensation, i.e., 7,10,14-trimethyl-2,9-B-norcardochrysadien-15-one (XV). When this ketone was hydrogenated in presence of a platinum catalyst, one molecule of hydrogen was absorbed and 7,10,14-trimethyl-9-B-norcardochrysanen-15-one (XVI) was formed:



(I) (XV) (XVI)

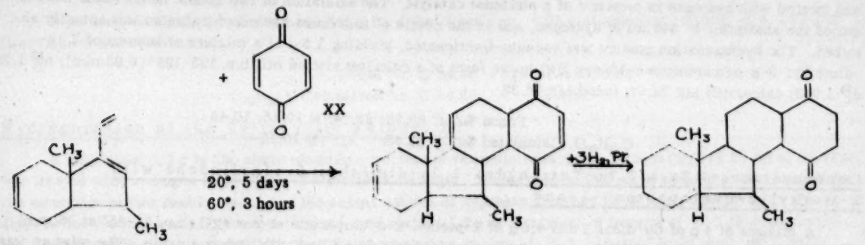
The condensation of the diene I with citraconic anhydride (XVII) was carried out at room temperature in benzene solution or by boiling with glacial acetic acid. In this condensation a very viscous oil was obtained, which did not crystallize when cooled to −35°; this, by analogy with other similar condensation reactions studied in our laboratory, should be a mixture of two isomeric anhydrides (XVIII and XIX):



(I) (XVII) (XVIII) (XIX)

A mixture of the corresponding acids was obtained in the form of a noncrystallizing oil by hydrolysis of the condensation product with alkali or aqueous acetic acid.

The condensation of the diene I with p-benzoquinone (XX) was effected by heating a mixture of the components in dioxane solution in a sealed glass tube at 60°. The condensation product formed pale-yellow crystals, m.p. 166° and consisted of 7,10-dimethyl-2,9,16-B-norcardochrysatriene-15,17a-dione (XXI). When this diketone was hydrogenated in presence of a platinum catalyst, three molecules of hydrogen were absorbed and the corresponding tetracyclic diketone (XXII) was formed; it formed colorless crystals, m.p. 141°.



(I) (XXI) (XXII)

In conclusion it must be pointed out that none of the tetracyclic ketones described in this paper give characteristic crystalline derivatives with semicarbazide, and, with the exception of the diketone XXI, which gives a normal

derivative, they all form products with 2,4-dinitrophenylhydrazine that have extended melting-point ranges and give a high nitrogen content in the analysis.

EXPERIMENTAL

1-Ethynyl-3a,4,7,8a-tetrahydro-3,7a-dimethyl-1-indanol

A solution of 9.2 g of sodium in 350 ml of liquid ammonia was placed in a three-necked flask fitted with mechanical stirrer and thermometer, and it was then stirred vigorously and cooled with dry ice (−70°) while a current of dry acetylene was passed at 20 liters per hour for three hours. Stirring of the sodium acetylide was continued and acetylene was passed (at 10 liters per hour) while a solution of 33 g of 3a,4,7,8a-tetrahydro-3-7a-dimethyl--1-indanone (b.p. 92-92.5° at 7 mm; n_D^{22} 1.4912) [1] in 75 ml of absolute ether was added at −70° over a period of 30 minutes, after which stirring and passage of acetylene was continued for one hour. The reaction mixture was left overnight in a bath of dry ice. On the next day practically the whole of the ammonia was removed, and additions were made of 100 ml of ether, 35 g of ammonium chloride, and 150 ml of water (from a dropping funnel). The ether layer was separated, and the aqueous layer was carefully extracted with ether. The product was washed with water, dried with sodium sulfate, and fractionated, yielding 33.4 g (87.4%) of 1-ethynyl-3a,4,7,8a-tetrahydro--3,7a-dimethyl-1-indanol, b.p. 88-90° at 3 mm; n_D^{21} 1.5070 [1].

The partial hydrogenation of this acetylenic alcohol in presence of a Pd catalyst (one molecule of hydrogen) yielded the previously described [1] 3a,4,7,8a-tetrahydro-3,7a-dimethyl-1-vinyl-1-indanol.

3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinylindene (I)

A mixture of 3 g of 3a,4,7,8a-tetrahydro-3,7a-dimethyl-1-vinyl-1-indanol (b.p. 88-90° at 3.5 mm; n_D^{20} 1.5045) and 1.5 g of freshly calcined, finely ground potassium hydrogen sulfate was heated at 120° for ten minutes under reduced pressure (95 mm). When cool, the mixture was carefully extracted with ether, the potassium hydrogen sulfate was filtered off, and the ethereal solution was washed with water, dried with calcium chloride, and fractionally distilled, yielding 2.2 g of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinylindene (I), b.p. 60-62° at 1.5 mm; n_D^{22} 1.5070 [1].

Condensation of 3a,4,7,7a-Tetrahydro-1-3a-dimethyl-3-vinylindene with 2-Cyclopenten -1-one

A mixture of 5 g of the diene I and 10 g of 2-cyclopenten -1-one (V) (b.p. 43-45° at 17 mm; n_D^{20} 1.4605) [4] was heated at 130° for 18 hours in a sealed glass tube filled with carbon dioxide. The mixture was then vacuum-fractionated, yielding 3 g of a mixture of tetracyclic ketones (VIII) in the form of a viscous yellow oil that did not crystallize when cooled to −35°; b.p. 132-134° (0.034 mm); n_D^{20} 1.5400; d_4^{20} 1.048; calculated MR 75.60; found MR 76.67.

Found %: C 84.30; 84.47; H 9.31, 9.37
$C_{15}H_{24}O$. Calculated %: C 84.31; H 9.45

Hydrogenation of the Tetracyclic Ketones VIII

A solution of 2 g of the above-described mixture of isomeric tetracyclic ketones (VIII) in 20 ml of dioxane was treated with hydrogen in presence of a platinum catalyst. The saturation of two double bonds would have required the absorption of 345 ml of hydrogen, and in the course of four hours 210 ml of hydrogen was actually absorbed. The hydrogenation product was vacuum-fractionated, yielding 1.5 g of a mixture of isomers of 7,10--dimethyl-9-B-norcardosteren-15-one (IX) in the form of a colorless viscous oil, b.p. 123-126° (0.03 mm); n_D^{20} 1.5288; d_4^{20} 1.043; calculated MR 76.07; found MR 76.33.

Found %: C 83.08; 83.14; H 10.45; 10.40
$C_{15}H_{24}O$. Calculated %: C 83.45; H 10.15

Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinylindene with 2-Methyl-2-cyclopenten -1-one

A mixture of 4 g of the diene I and 4.8 g of 2-methyl-2-cyclopenten -1-one (XI) (b.p. 53-55° at 15 mm; n_D^{20} 1.4756) [4] was heated at 170° for ten hours in a sealed glass tube filled with carbon dioxide. The mixture was then vacuum-fractionated, yielding 1.5 g of a mixture of the isomeric tetracyclic ketones X in the form of a viscous yellow oil that did not crystallize when cooled to −35°; it had b.p. 133-138° (0.03 mm); n_D^{20} 1.5380; d_4^{20} 1.037; calculated MR 80.29; found MR 81.40.

Found %: C 85.85; 85.75; H 10.01; 9.95
$C_{15}H_{24}O$. Calculated %: C 84.40; H 9.70

Hydrogenation of the Tetracyclic Ketones X

A solution of 1.3 g of the above-described mixture of isomeric tetracyclic ketones (X) in 15 ml of dioxane was treated with hydrogen in presence of a platinum catalyst. Theoretically, 225 ml of hydrogen was required for the saturation of two double bonds, and actually 225 ml of hydrogen was absorbed in 20 minutes. The hydrogenation product was vacuum-fractionated and yielded 1 g of a mixture of isomers of 7,10,14-trimethyl-9-B-norcardosteren--15-one (XI) in the form of a very viscous colorless liquid, b.p. 140-142° (0.04 mm); n_D^{20} 1.5280; d_4^{20} 1.019; calculated MR 80.70; found MR 82.25.

Found %: C 84.49; 84.52; H 10.80; 10.68
$C_{19}H_{28}O$. Calculated %: C 83.76; H 10.40

Condensation of 3a,4,7,7a-Tetrahydro-1-3a-dimethyl-3-vinylindene with 2-Cyclohexen-1-one

A mixture of 5 g of the diene I and 50 g of the 2-cyclohexen-1-one (VII) (b.p. 67° at 19 mm; n_D^{20} 1.4850) [4] was heated at 170° for ten hours in a sealed glass tube filled with carbon dioxide. The mixture was then vacuum-fractionated, and yielded 3 g of the isomeric tetracyclic ketones XII in the form of a yellow viscous oil, which did not crystallize when cooled to −35°; it had b.p. 150.5-151° (at 0.07 mm); n_D^{20} 1.5375; d_4^{20} 1.0533; calculated MR 80.22; found MR 80.12.

Found %: C 84.10; 83.96; H 9.96; 10.13
$C_{19}H_{28}O$. Calculated %: C 84.40 H 9.70

Hydrogenation of the Tetracyclic Ketones XII

A solution of 1.5 g of the above-described mixture of isomeric tetracyclic ketones (XII) in 15 ml of dioxane was treated with hydrogen in presence of a platinum catalyst. Theoretically, 248 ml of hydrogen was required for the saturation of two double bonds, and the actual volume of hydrogen absorbed in one hour was 200 ml. The hydrogenation product was vacuum-fractionated, and yielded 1.2 g of a mixture of isomers of 7,10-dimethyl-9-B-norcardochrysanen-15-one (XIII) in the form of a colorless viscous oil, b.p. 132-134.5° (0.035 mm); n_D^{20} 1.5215; d_4^{20} 1.0433; calculated MR 80.70; found MR 79.51.

Found %: C 83.13; 82.92; H 10.75; 10.56
$C_{19}H_{28}O$. Calculated %: C 83.76; H 10.40

Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinylindene with 2-Methyl-2-cyclohexen-1-one

A mixture of 4 g of the diene I and 45 g of 2-methyl-2-cyclohexen-1-one (XIV) (b.p. 64-64.5° at 15 mm; n_D^{20} 1.4802) [4] was heated at 170° for ten hours in presence of 0.5 g of dimethylaniline in a sealed glass tube. The mixture was then vacuum-fractionated, and yielded 2.5 g of a mixture of the isomeric tetracyclic ketones XV in the form of a viscous yellow oil, b.p. 147-150° (0.032 mm); n_D^{20} 1.5415; d_4^{20} 1.056; Calculated MR 84.84; Found MR 84.60.

Found %: C 85.05, 85.06; H 10.03, 9.89
$C_{20}H_{28}O$. Calculated %: C 84.45; H 9.92

After long standing, the oil obtained partially crystallized out: 0.25 g of colorless crystals, m.p. 139-142° (from ether) was obtained.

Found %: C 84.46, 84.21; H 9.93, 9.84
$C_{20}H_{28}O$. Calculated %: C 84.45; H 9.92

Hydrogenation of the Tetracyclic Ketones XV

A solution of 1.3 g of the above-described mixture of isomeric tetracyclic ketones (XV) in 10 ml of dioxane was treated with hydrogen in presence of a platinum catalyst. Theoretically, 205 ml of hydrogen was required for the saturation of two double bonds, and the actual volume of hydrogen absorbed in 15 hours was 107 ml. The hydrogenation product was vacuum-fractionated, and yielded 1.2 g of a mixture of isomers of 7,10,14-trimethyl-9-B-norcardochrysanen-15-one (XVI) in the form of a colorless viscous oil, b.p. 148-150° (0.07 mm); n_D^{20} 1.5288; d_4^{20} 1.033; Calculated MR 85.23; Found MR 85.43.

Found %: C 83.72, 83.88; H 10.70, 10.62
$C_{20}H_{30}O$. Calculated %: C 83.86; H 10.50

Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinylindene with Citraconic Anhydride

A mixture of 5.1 g of the diene I, 3.8 g of citraconic anhydride (XVII) (n_D^{20} 1.4712), and 1 ml of dry benzene was set aside for five days at room temperature. The residue after removal of benzene was vacuum-fractionated, and yielded 3.5 g of a mixture of isomeric anhydrides (XVIII and XIX) in the form of a very viscous yellow oil, which did not crystallize when cooled to − 35° and then rubbed out with various organic solvents; it had b.p. 144-145° (0.012 mm); n_D^{20} 1.5310; d_4^{20} 1.137; Calculated MR 77.25; Found MR 77.88.

Found %: C 75.87, 75.66; H 7.80, 7.86

$C_{18}H_{22}O_3$. Calculated %: C 75.50; H 7.75

Hydrolysis of this product with alcoholic alkali or 50% acetic acid resulted in the formation of a noncrystallizing mixture of acids.

Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinylindene with p-Benzoquinone

A solution of 2 g of the diene I and 1 g of p-benzoquinone (m.p. 116°) in 20 ml of dioxane was sealed in a glass tube filled with carbon dioxide, left at room temperature for one day, and then heated at 60° for three hours. The residue that remained after removal of dioxane under somewhat reduced pressure (100-110 mm) partially crystallized, and 1.8 g of yellowish crystals of the tetracyclic diketone XXI, m.p. 155-159° was filtered off. After two recrystallizations from methanol the product melted at 166-166.5°.

Found %: C 80.93, 80.69; H 8.30, 8.02

$C_{19}H_{22}O_2$. Calculated %: C 80.79; H 7.86

The 2,4-dinitrophenylhydrazone melted at 213-215°.

Found %: N 11.64, 12.26

$C_{25}H_{24}O_5N_4$. Calculated %: N 12.12

Hydrogenation of the Adduct

A solution of 0.75 g of crystals of m.p. 166-166.5° in 10 ml of dioxane was treated with hydrogen in presence of a platinum catalyst. Theoretically, 180 ml of hydrogen was required for the saturation of three double bonds, and in 15 minutes 190 ml of hydrogen was actually absorbed. The dioxane was removed under reduced pressure (110 mm), and the residue crystallized. Filtration yielded 0.7 g of crystals of 7,10-dimethyl-B-norcardochrysane-15,-17a-dione (XXII), m.p. 132-135.5°, which after two recrystallizations from ether melted at 140.5-141°.

Found %: C 78.92, 78.95; H 9.49, 9.61

$C_{19}H_{28}O_2$. Calculated %: C 79.11; H 9.80

SUMMARY

1. 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinylindene (I) has been caused to undergo the diene condensation with 2-cyclopenten-1-one (V), 2-methyl-2-cyclopenten-1-one (VI), 2-cyclohexen-1-one (VII), 2-methyl-2-cyclohexen-1-one (XIV), p-benzoquinone, and citraconic anhydride.

2. In this way 30-40% yields have been obtained of the corresponding tetracyclic steroid ketones VIII, X, XII, XV, and XXI, which have B-norcardosterane and B-norcardochrysane skeletons.

Received October 7, 1952.

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[3] I. N. Nazarov et al., Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5, 901, 920, 929 (1953). ***

[4] I. N. Nazarov et al., Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5, 889 (1953).****

* See Consultants Bureau Translation, page 911

** See Consultants Bureau Translation, page 651

*** See Consultants Bureau Translation, page 799, 817, 827

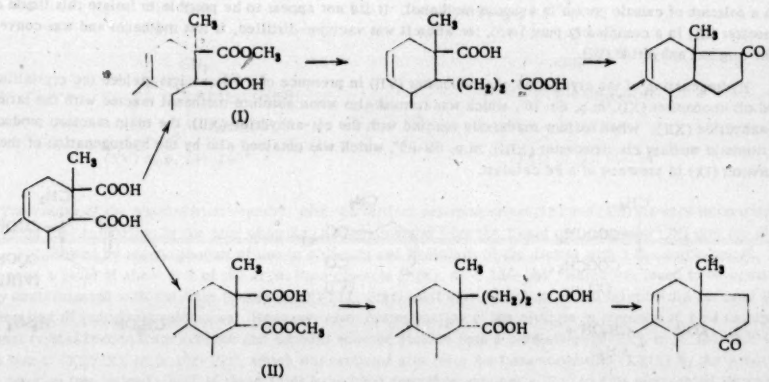
**** See Consultants Bureau Translation, page 787

SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO STEROIDS

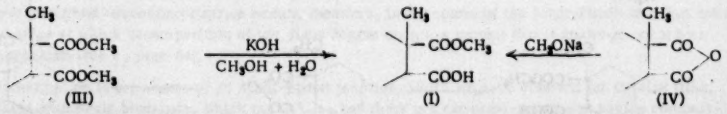
COMMUNICATION XXII. STEREOCHEMISTRY OF POLYCYCLIC COMPOUNDS. II. MONOESTERS OF THE CIS AND TRANS FORMS OF 1-METHYL-1,2-CYCLOHEXANEDICARBOXYLIC AND 1-METHYL-4-CYCLOHEXENE-1,2-DICARBOXYLIC ACIDS, AND THEIR REACTIONS*

I. N. Nazarov and V. F. Kucherov

For the synthesis of polycyclic compounds related to steroids from cyclic 1,2-dicarboxylic acids by lengthening of a carbon chain followed by cyclization, it is necessary to have the corresponding monoesters of types (I) and (II).



Having developed an accessible method for the synthesis of anhydrides and diesters of cis and trans forms of 1-methyl-1,2-cyclohexanedicarboxylic acid and 1-methyl-4-cyclohexene-1,2-dicarboxylic acid [1], we have made a detailed study, for these model cases, of various methods for the preparation of monoesters of types (I) and (II). Monoesters of type (I), applicable to the synthesis of steroid compounds, can be prepared either by the partial hydrolysis of diesters (III) with one equivalent of alkali in aqueous methanol [2], or by the action of sodium alkoxide on an alcoholic solution of the anhydride (IV) [3, 4]



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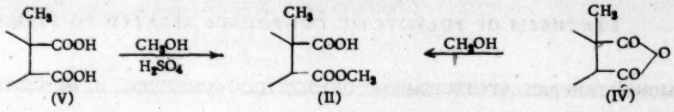
By these methods it is generally possible to prepare monoesters in which the carboxyl group on the tertiary carbon atom is esterified.

On the other hand, by the action of alcohol on anhydrides (IV) [5], or by partial esterification of the corresponding dicarboxylic acids (V), monoesters of type (II) are preferentially formed; these have a free carboxyl group on the tertiary carbon atom

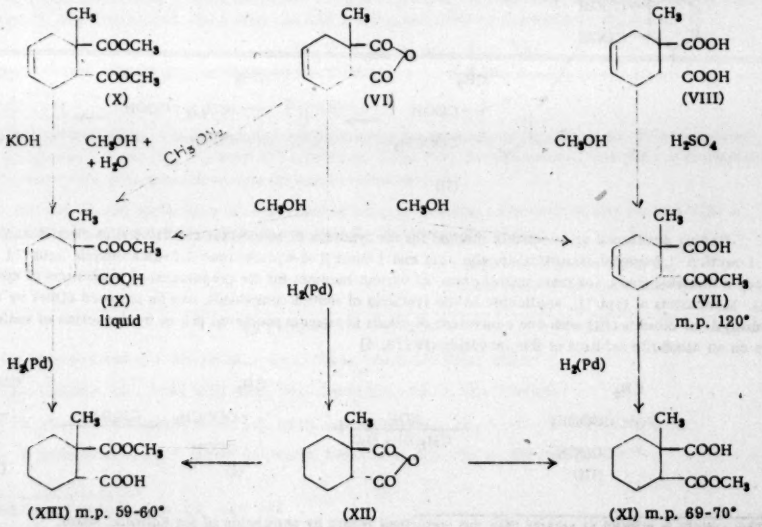


We have made a detailed study of all of these methods for the very simple model examples of cis- and trans-1-methyl-1,2-cyclohexanedicarboxylic and -1-methyl-4-cyclohexene-1,2-dicarboxylic acids, and we have obtained the following results.

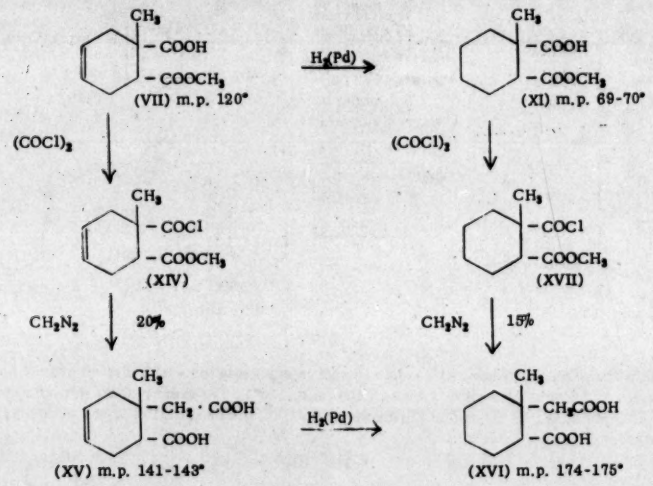
When the anhydride of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (VI) was boiled with absolute methanol, a mixture of isomeric monoesters (VII and IX) of the cis series was obtained, the former predominating. By treatment of this mixture with petroleum ether and freezing out, a yield of about 45% of the pure crystalline secondary cis-monoester VII, m.p. 120-121°, was obtained. The same monoester in satisfactory yield was obtained also by the partial esterification of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (VIII).

The isomeric liquid tertiary cis-monoester (IX) was obtained as main product when the cis-anhydride (VI) was heated with a solution of sodium methoxide in methanol, and also by the partial hydrolysis of the diester (X) with a solution of caustic potash in aqueous methanol. It did not appear to be possible to isolate this liquid cis-monoester (IX) in a completely pure form, for when it was vacuum-distilled, it lost methanol and was converted into the original anhydride (VI).

Hydrogenation of the crystalline cis-monoester (VII) in presence of a Pd catalyst yielded the crystalline saturated cis-monoester (XI), m.p. 69-70°, which was formed also when absolute methanol reacted with the saturated cis-anhydride (XII). When sodium methoxide reacted with the cis-anhydride (XII), the main reaction product was the isomeric tertiary cis-monoester (XIII), m.p. 59-60°, which was obtained also by the hydrogenation of the liquid monoester (IX) in presence of a Pd catalyst.



In order to prove the structures of the cis-monoesters obtained, they were converted into the corresponding acetic acid derivatives by Arndt-Eistert lengthening of the carbon chain. With oxalyl chloride, the monoester (VII) gave the acid chloride (XIV) in quantitative yield, and this, when treated with excess of diazomethane, was converted into a diester, which was hydrolyzed to the cis-acid (XV). Owing to steric hindrance, this reaction did not go smoothly, and the acid (XV) was obtained in low yield (about 20%). Hydrogenation of the acid (XV) in presence of a Pd catalyst yielded the known cis-2-carboxy-1-methylcyclohexaneacetic acid (XVI), m.p. 174-175° [6]. A low yield (about 15%) of the same acid was obtained also from the unsaturated monoester (XI) via the acid chloride (XVII) by the Arndt-Eistert reaction:

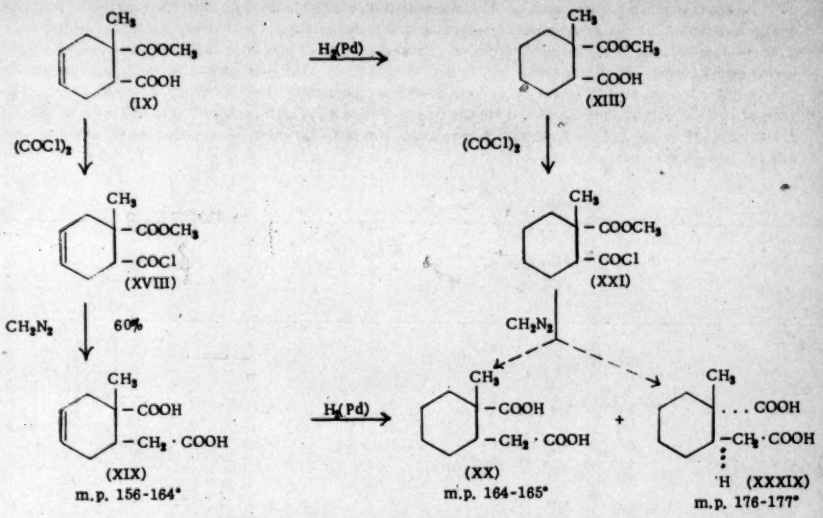


The course of the Arndt-Eistert reaction with the tertiary cis-monoesters (IX) and (XIII) is very interesting. It was found that conversion of the acid chloride (XVIII) obtained from the liquid cis-monoester (IX) into the diazoketone, followed by rearrangement of this to a diester and hydrolysis of the diester with 20% caustic potash, finally gave a yield of about 60% of the crystalline cis-acid (XIX), m.p. 156-164°, which was found to be considerably contaminated with the trans isomer (XXXVIII). Fractional crystallization of this mixture did not lead to the separation of individual substances. However, after hydrogenation of the mixture in presence of a Pd catalyst, fractional crystallization from acetone and aqueous acetone yielded both a pure cis-acid (XX), m.p. 164-165° and a trans isomer (XXXIX), m.p. 176-177°, which was prepared also from the trans-monoester (XXIX) by the Arndt-Eistert reaction (see below). Both of these acids have been described previously [2, 7]. This unexpected stereoisomerization in the Arndt-Eistert reaction was confirmed by us in the case of the pure saturated crystalline cis-monoester (XIII).

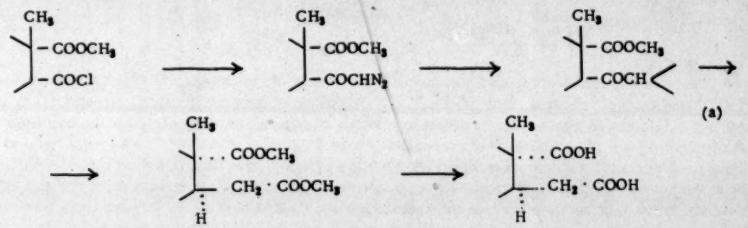
When the Arndt-Eistert reaction was carried out on the cis-acid chloride (XXI) obtained from the cis-monoester, a crystalline mixture of approximately equal amounts of the cis-acid (XX), m.p. 164-165°, and the trans-acid (XXXIX), m.p. 176-177°, was obtained, and these substances were isolated in the pure form by fractional crystallization. There can be no doubt that the original acid chloride (XXI) belongs to the cis series: it was quantitatively hydrolyzed into pure cis-1-methyl-1,2-cyclohexanedicarboxylic acid.

The above-described stereoisomerization occurs, therefore, in the course of the Arndt-Eistert reaction, most probably at the stage at which decomposition of the diazo ketone occurs, a process that is known to occur by a free radical mechanism (see a, page 54).

Stereoisomerization in the course of an Arndt-Eistert reaction, which we have observed for the first time, may be associated with steric hindrance, which may exist when there is a cis-ortho-substituent having comparatively large bulk. We have shown that such steric effects occur in the formation of anilides. It was found that the



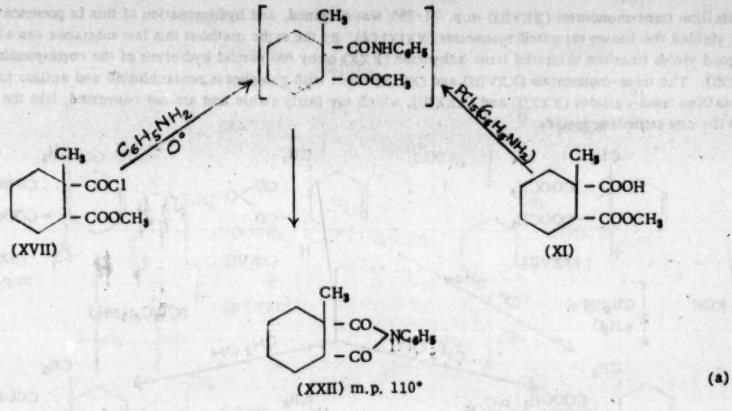
isomeric cis-acid chlorides (XVII) and (XXI), when treated in ether solution with excess of aniline at 15-20°, gave quantitative yields of the same crystalline amide (XXII) (m.p. 110°). The same product was obtained directly from the monoesters (XI) and (XIII) by the action of phosphorus pentachloride and aniline in the usual way [6]. In the



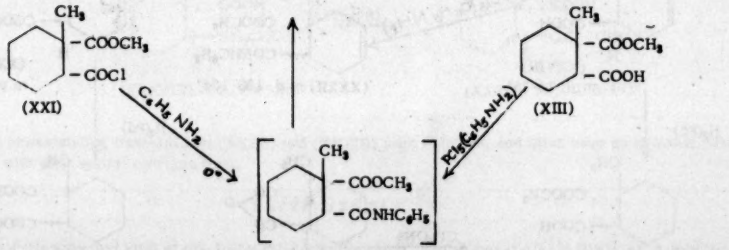
reaction of aniline with the acid chlorides (XVII) and (XXI), even under very mild conditions (0°), it was not found possible to isolate the corresponding anilides, which are apparently unable to exist, being spontaneously and completely converted into the imide (XXII) owing to the spatial proximity of the cis-ortho-methoxycarbonyl and anilide groups (see a, page 55).

The analogous reactions were investigated also for the cis-monoesters (VII) and (IX), which contain a double bond in the cyclohexane ring.

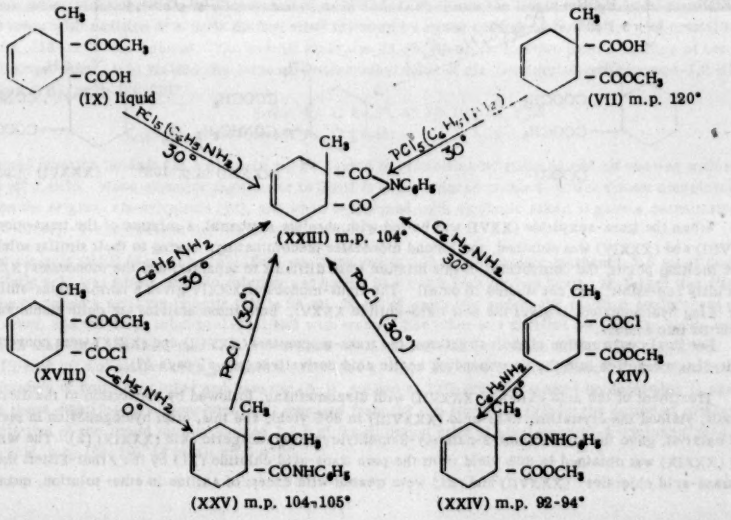
Both the monoesters (VII) and (IX) themselves, and also their acid chlorides (XIV and XVIII), give the same crystalline imide (XXIII), m.p. 103-104°, when treated with aniline at 20-30°. When, however, the acid chlorides (XIV) and (XVIII) reacted with aniline in ether solution at 0°, the corresponding crystalline anilides (XXIV and XXV) were isolated. They were quantitatively converted into the above-described crystalline imide (XXIII) when warmed in ether solution and with a small amount of phosphoryl chloride. This fact, which indicates the exceptionally high instability of the cis-anilides (XXIV) and (XXV), may be explained only by the spatial proximity of the methoxycarbonyl and anilide groups in the cis-ortho-positions. This is particularly evident from the examination of models, and it is confirmed by the fact of the ready formation of the imide of 1,2-cyclohexanedicarboxylic acid when the monoamide of this acid is heated [8].



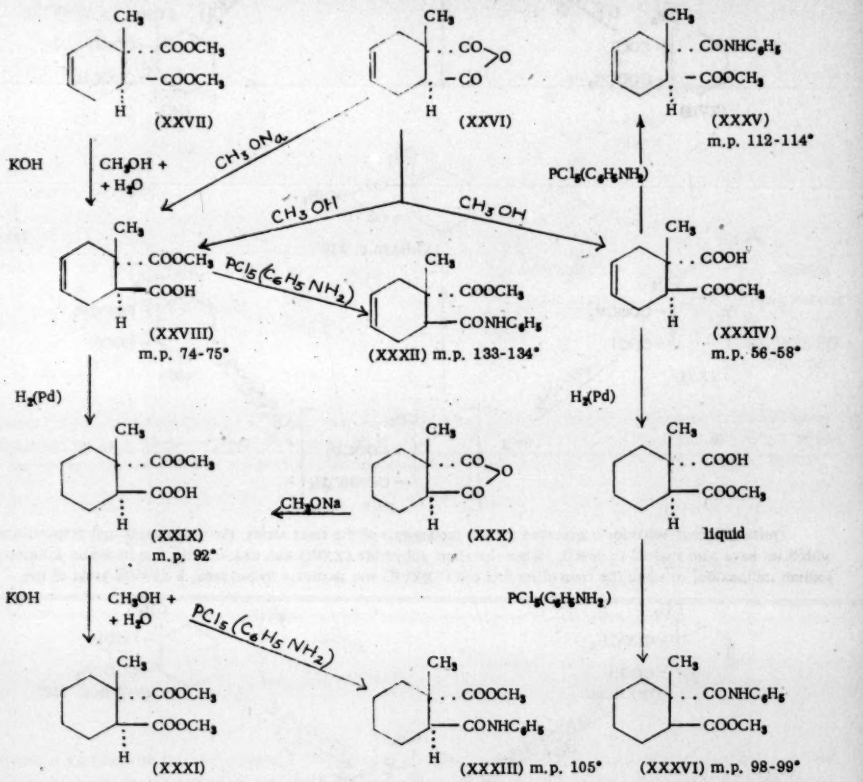
(a)



Quite different behavior is observed for the monoesters of the trans series, the preparation and properties of which we have also studied in detail. When the trans-anhydride (XXVI) was treated with a methanolic solution of sodium methoxide, or when the trans-dimethyl ester (XXVII) was partially hydrolyzed, a 60-70% yield of the



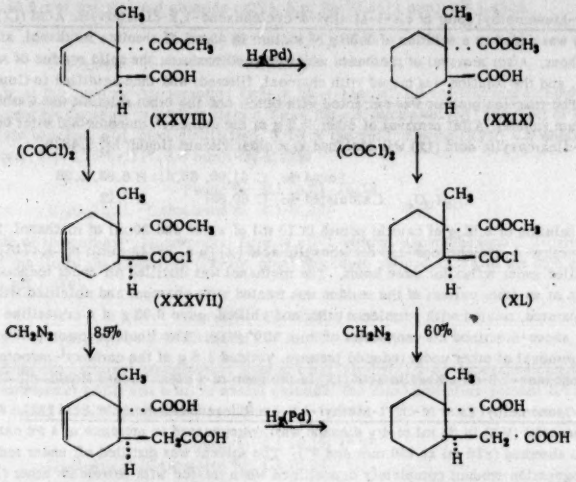
crystalline trans-monoester (XXVIII) m.p. 74-75°, was obtained, and hydrogenation of this in presence of a Pd catalyst yielded the known saturated monoester (XXIX) [2]. By the same methods this last substance can also be obtained in good yields from the saturated trans-anhydride (XXX) or by the partial hydrolysis of the corresponding trans-ester (XXXI). The trans-monoesters (XXVIII) and (XXIX) react with phosphorus pentachloride and aniline to give the crystalline trans-anilides (XXXII) and (XXXIII), which are fairly stable and are not converted, like the cis-anilides, into the corresponding imides.



When the trans-anhydride (XXVI) was boiled with absolute methanol, a mixture of the trans-monoesters (XXVIII) and (XXXIV) was obtained, the second monoester predominating. Owing to their similar solubilities and close melting points, the components of this mixture were difficult to separate, and the monoester (XXXIV) being difficultly accessible, was not studied in detail. The trans-monoester XXXIV gives a normal trans-anilide (XXXV); after being hydrogenated, it gives the new trans-anilide XXXVI. Both these anilides are quite stable and are not converted into amides.

For final confirmation of their structures, the trans-monoesters (XXVIII) and (XXIX) were converted by the Arndt-Eistert reaction into the corresponding acetic acid derivatives (see a, page 57).

Treatment of the acid chloride (XXXVII) with diazomethane, followed by conversion to the diester and hydrolysis, yielded the crystalline trans-acid (XXXVIII) in 85% yield, and this, after hydrogenation in presence of a Pd catalyst, gave the known trans-2-carboxy-2-methylcyclohexaneacetic acid (XXXIX) [2]. The same trans-acid (XXXIX) was obtained in 60% yield from the pure trans-acid chloride (XL) by the Arndt-Eistert method. When the trans-acid chlorides (XXXVII) and (XL) were treated with excess of aniline in ether solution, quantitative



yields of the corresponding trans-anilides (XXXII) and (XXXIII) were obtained, and these were quite stable, which is in accord with their spatial configurations.

EXPERIMENTAL

carboxy^2-Monomethyl Ester of cis-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (VII). a) A solution of 25 g of the cis-anhydride (VI) [b.p. 113-115° (4 mm); n_D^{20} 1.4890] [1] in 75 ml of absolute methanol was boiled under reflux for six hours. The methanol was distilled off under reduced pressure, and there remained a viscous liquid, which partially crystallized when treated with petroleum ether. The crystalline product was filtered off and washed with petroleum ether, yielding 12.2 g of a substance of m.p. 115-118°. From the liquid residue, after dissolution in petroleum ether with addition of a little diethyl ether followed by strong cooling, a further 1.3 g of crystalline substance, m.p. 113-115°, was isolated. The overall yield was 46.5%. Recrystallization from a mixture of benzene and petroleum ether (1:5) yielded the carboxy^2-monomethyl ester of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (VII), m.p. 120-121°.

	Found %:	C 60.77, 60.89; H 7.04, 6.98
$C_{10}H_{14}O_4$.	Calculated %:	C 60.65; H 7.12

The liquid reaction product (16.1 g) could not be caused to crystallize by standing and by treating with solvents; it had n_D^{20} 1.4875. When attempts were made to distil it under reduced pressure, it was almost completely converted into the original cis-anhydride (VI), and when hydrolyzed with alcoholic alkali it gave a quantitative yield of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (VIII).

b) The cis-acid (VIII) (4 g; m.p. 167-168°) was dissolved in 100 ml of absolute methanol, 2.6 ml of concentrated sulfuric acid was added, and the solution was boiled in a water bath for two hours. Methanol was distilled off under reduced pressure until the volume fell to 25 ml, 30 ml of water was added, the reaction product was extracted with ether, and the ether solution was washed with water. The ether was distilled off, and the liquid esterification product that then remained partially crystallized when treated with petroleum ether. The crystalline product was filtered off and washed with petroleum ether (2.4 g, m.p. 105-110°). The product, after crystallization from a mixture of petroleum ether and benzene (5:1), melted at 119-120° and showed no depression in admixture with the above-described cis-monoester (VII) prepared from the cis-anhydride (VI) by the action of methanol. Vacuum distillation of the liquid residue yielded 1.2 g of the dimethyl ester of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid, b.p. 104-106° (4 mm); n_D^{20} 1.4725.

carboxy[1]-Monomethyl Ester of cis-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (IX). a) The cis-anhydride (XI) (5 g) was added to a solution of 1.35 g of sodium in 40 ml of absolute methanol, and the mixture was boiled for one hour. After removal of methanol under reduced pressure, the solid residue of salts was dissolved in 20 ml of water, and the solution was mixed with charcoal, filtered, and then acidified to Congo red with hydrochloric acid. The reaction product was extracted with ether, and the ether solution was washed with water and dried with sodium sulfate. After removal of ether, 5.2 g of the carboxy[1]-monomethyl ester of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (IX) was obtained as a clear viscous liquid; n_D^{20} 1.4870.

	Found %:	C 61.00, 60.81; H 6.93, 6.93
$C_{10}H_{14}O_4$.	Calculated %:	C 60.65; H 7.12

b) To a solution of 0.55 g of caustic potash in 10 ml of water and 30 ml of methanol, 2 g of the dimethyl ester of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (X) [b.p. 98° (2 mm); n_D^{20} 1.4746] was added, and the mixture was boiled under reflux for three hours. The methanol was distilled off under reduced pressure, and an aqueous solution of an ether extract of the residue was treated with charcoal and acidified with hydrochloric acid. The oil that separated, treated with petroleum ether and chilled, gave 0.03 g of a crystalline substance, which was found to be the above-described cis-monoester of m.p. 120° (VII). The liquid reaction product, after extraction with ether and removal of ether under reduced pressure, yielded 1.8 g of the carboxy[1]-monomethyl ester of cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (IX) in the form of a clear viscous liquid; n_D^{20} 1.4870.

carboxy[2]-Monomethyl Ester of cis-1-Methyl-1,2-cyclohexenedicarboxylic Acid (XI). a) A solution of 5.5 g of the cis-monoester (VII) in 35 ml of dry dioxane was hydrogenated in presence of a Pd catalyst. One molecule of hydrogen was absorbed (625 ml at 760 mm and 0°). The solvent was distilled off under reduced pressure, and the liquid hydrogenation product completely crystallized when treated with petroleum ether (5.1 g, m.p. 67-69°). Crystallization of petroleum ether yielded the carboxy[2]-monomethyl ester of cis-1-methyl-1,2-cyclohexanedicarboxylic acid (XI), which had a constant melting point, 69-70°.

	Found %:	C 60.22, 59.94; H 8.32, 8.11
$C_{10}H_{16}O_4$.	Calculated %:	C 60.0; H 8.05

b) A solution of 3 g of the cis-anhydride (XII) in 20 ml of absolute methanol was boiled for five hours. The methanol was distilled off under reduced pressure, and the liquid mixture of monoesters was dissolved in petroleum ether and set aside to crystallize after being seeded with some pure monoester (XI). The product, 0.8 g of the crystalline monoester (XI), m.p. 65-68°, melted at 69-70° after recrystallization from petroleum ether and showed no depression in melting point when mixed with the previous sample.

carboxy[1]-Monomethyl Ester of cis-1-Methyl-1,2-cyclohexanedicarboxylic Acid (XIII). a) The cis-anhydride (XII) (3.5 g) was added to a warm solution of 1 g of sodium in 25 ml of absolute methanol, and the solution was boiled in a water bath for three hours. The methanol was distilled off under reduced pressure, and the residue of salts was dissolved in 10 ml of water and acidified with hydrochloric acid. The viscous semicrystalline product that separated was extracted with ether, and the extract was dried with sodium sulfate. The ether was driven off, and the residue was dissolved in a small amount of petroleum ether by application of heat, and was set aside to crystallize while cooling. The product was 2.35 g of crystals, m.p. 57-58°. From the mother liquor, after removal of part of the solvent followed by strong cooling, a further 0.55 g of crystals was isolated (m.p. 56-58°). The overall yield was 69%. After being recrystallized from petroleum ether, the carboxy[1]-monomethyl ester of cis-1-methyl-1,2-cyclohexanedicarboxylic acid (XIII) melted at 59-60°.

	Found %:	C 60.03, 60.06; H 8.12, 8.09
$C_{10}H_{16}O_4$.	Calculated %:	C 60.0; H 8.05

b) A solution of 3 g of the liquid monoester (IX) in 20 ml of dioxane was treated with hydrogen in presence of a Pd catalyst, and 340 ml of hydrogen (760 mm, 0°) was absorbed. The solvent was distilled off under reduced pressure, and the viscous liquid hydrogenation product was dissolved in a small amount of petroleum ether, from which, on cooling, 2.1 g of the crystalline cis-monoester (XIII), m.p. 58-59° and identical with the previous sample, was isolated.

Preparation of Acid Chlorides of cis-Monoesters

1. Acid Chloride of the carboxy[2]-Monomethyl Ester of cis-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (XIV). Oxalyl chloride (10 ml) was added to a solution of 10 g of the cis-monoester (VII) in 100 ml of absolute benzene, and the mixture was set aside for one hour at room temperature. It was then heated for 30 minutes at 40-45°, and the benzene and excess of oxalyl chloride were distilled off. The liquid reaction product was vacuum-

distilled, and yielded 10.6 g of the cis-acid chloride (XIV), b.p. 99-99.5° (1 mm); n_D^{22} 1.4905.

Found %: Cl 16.41, 16.43
$C_{10}H_{13}O_3Cl$. Calculated %: Cl 16.35

2. Acid Chloride of the carboxy²-Monomethyl Ester of cis-1-Methyl-1,2-cyclohexanedicarboxylic Acid (XVII). This was prepared by the same procedure from 5.7 g of the cis-monoester (XI) and 6 ml of oxalyl chloride in 60 ml of absolute benzene, and, after distillation, 5.7 g of the acid chloride (XVII) was obtained in the form of a colorless liquid, b.p. 110.5-111° (3.5 mm); n_D^{20} 1.4780.

Found %: Cl 16.21, 16.18
$C_{10}H_{13}O_3Cl$. Calculated %: Cl 16.17

3. Acid Chloride of the carboxy¹-Monomethyl Ester of cis-1-Methyl-4-cyclohexene-1,2-carboxylic Acid (XVIII). From 13 g of the liquid cis-monoester (IX) the usual procedure yielded 13.3 g of the acid chloride XVIII, b.p. 96-97° (1.5 mm); n_D^{22} 1.4865.

Found %: Cl 16.52, 16.65
$C_{10}H_{13}O_3Cl$. Calculated %: Cl 16.35

4. Acid Chloride of the carboxy¹-Monomethyl Ester of cis-1-Methyl-1,2-cyclohexanedicarboxylic Acid (XXI). From 3.8 g of the cis-monoester (XIII) and 5 ml of oxalyl chloride, the usual procedure yielded 3.7 g of the pure acid chloride (XXI), b.p. 112-112.5° (4 mm); n_D^{22} 1.4760.

Found %: Cl 16.19, 16.26
$C_{10}H_{13}O_3Cl$. Calculated %: Cl 16.17

cis-6-Carboxy-1-methyl-3-cyclohexene-1-acetic Acid (XV). A solution of 2 g of the cis-acid chloride (XIV) in 10 ml of absolute ether was added slowly with cooling to a dry ethereal solution of 2.1 g of diazomethane, and the mixture was set aside at room temperature for 24 hours. The ether was distilled off under reduced pressure, and the liquid residue of diazo ketone was dissolved with cooling in 45 ml of absolute methanol. Freshly prepared silver oxide (0.5 g) was added, and the mixture was boiled under reflux for six hours. The silver oxide was filtered off and washed with methanol. Methanol was distilled off under reduced pressure, and the liquid residue was hydrolyzed by treatment at the boil with 7 ml of 40% caustic potash and 5 ml of methanol for four hours. The methanol was distilled off, and the aqueous alkaline solution was treated with charcoal, filtered, and acidified with hydrochloric acid. The liquid reaction product separated and was extracted with ether. The ether extract was washed with water and dried, and the ether was driven off. The residue was dissolved in a small amount of acetone and the solution obtained was diluted with an equal volume of petroleum ether and allowed to stand, when a crystalline substance slowly separated. It was filtered off and washed with a mixture of acetone and petroleum ether (1:3). The product was 0.35 g of cis-6-carboxy-1-methyl-3-cyclohexene-1-acetic acid (XV), m.p. 136-140°. After recrystallization from a mixture of acetone and petroleum ether, the acid melted at 141-143°.

Found %: C 60.94, 60.80; H 7.11, 7.28
$C_{10}H_{14}O_4$. Calculated %: C 60.6; H 7.12

cis-2-Carboxy-1-methylcyclohexaneacetic Acid (XVI). a) A solution of 2.1 g of the cis-acid chloride (XVII) in 20 ml of absolute ether was added slowly with cooling to a dry ethereal solution of 2.1 g of diazomethane, and the mixture was set aside for 15 hours at room temperature. The ether was distilled off under reduced pressure, and the viscous residue was dissolved in 40 ml of absolute methanol. Silver oxide (0.5 g) was then added to the mixture, which was boiled for eight hours. The mixture was filtered, the methanol was distilled off under reduced pressure, and the residue was boiled with 10 ml of 40% caustic potash and 7 ml of methanol. The warm solution was treated with charcoal and filtered, the methanol was distilled off under reduced pressure, and the residue was acidified with hydrochloric acid. The oil that separated was extracted with ether, the extract was washed with water, and the ether was distilled off. The residue was dissolved in a small amount of acetone, and an equal volume of petroleum ether was added. A crystalline product (0.28 g) came down after a time, and this, after recrystallization from a mixture of acetone and petroleum ether, melted at 174-175°. The literature [5] gives 172-173° for the melting point of cis-2-carboxy-1-methylcyclohexaneacetic acid.

Found %: C 59.87, 59.95; H 8.04, 8.10
$C_{10}H_{14}O_4$. Calculated %: C 60.0; H 8.05

b) A solution of 0.1 g of cis-6-carboxy-1-methyl-3-cyclohexane-1-acetic acid (XV) in absolute methanol was treated with hydrogen in presence of a Pd catalyst. The methanol was distilled off, and from the crystalline

product, after recrystallization from a mixture of acetone and petroleum ether, an acid was obtained that melted at 174-175° and showed no melting-point depression in admixture with the cis-acid (XVI) described above.

Reaction of the cis-Acid Chloride (XVIII) with Diazomethane. A solution of 5 g of the cis-acid chloride (XVIII) in 20 ml of absolute ether was added slowly to a dry ethereal solution of diazomethane prepared from 25 g of methylnitrosourea, and the mixture was set aside at room temperature for 24 hours. The ether was distilled off under reduced pressure, the residue was dissolved in 100 ml of methanol with cooling, 1 g of freshly prepared silver oxide was added, and the mixture was boiled for six hours. In the early stages of heating vigorous evolution of nitrogen was observed. A further 0.3 g of silver oxide was added, and boiling was continued for a further two hours. The mixture was treated with charcoal and filtered, the methanol was removed under reduced pressure, and the liquid residue was hydrolyzed by boiling it with 25 ml of 40% caustic potash and 20 ml of methanol for six hours. The dark-colored solution was treated with charcoal and filtered, the methanol was distilled off under reduced pressure, and the residue was acidified with hydrochloric acid. A yellow partially solid reaction product was precipitated, and this practically completely solidified when cold. The crystalline product was filtered off and washed free from yellow resin with 50% aqueous acetone. The product was 2.6 g of acid, m.p. 157-163°, and from the aqueous solution and washings a further 0.2 g of the acid, m.p. 155-163°, was separated, the total yield being 60%. After repeated crystallizations from acetone, aqueous acetone, or a mixture of acetone and petroleum ether, crystals were obtained having an indefinite melting point (162-166°) and corresponding in analysis to 6-carboxy-6-methyl-3-cyclohexene-1-acetic acid (XIX).

Found %: C 60.86, 60.89; H 7.35, 7.32

$C_{10}H_{14}O_4$. Calculated %: C 60.6; H 7.12

The acid obtained (XIX, 1 g), m.p. 162-166°, was hydrogenated in 15 ml of absolute methanol in presence of a Pd catalyst. After removal of solvent, a clear viscous liquid was obtained, and this crystallized out when treated with petroleum ether and had m.p. 130-145°. The hydrogenation product was recrystallized from a mixture of acetone and petroleum ether (1:1), and 0.3 g of substance melting at 157-161° was obtained. After a further recrystallization it melted at 164-165°, the melting point of known cis-2-carboxy-2-methylcyclohexaneacetic acid (XX).

Found %: C 59.95, 60.0; H 8.19, 8.02

$C_{10}H_{16}O_4$. Calculated %: C 60.0; H 8.05

From the mother liquor, after two crystallizations from acetone, a small amount of a crystalline substance of m.p. 175-177° was isolated; it showed no melting-point depression in admixture with trans-2-carboxy-2-methylcyclohexaneacetic acid (XXXIX) (see below).

Reaction of the cis-Acid Chloride (XXI) with Diazomethane. A solution of 3.0 g of the cis-acid chloride (XXI) in 20 ml of absolute ether was added slowly under cooling to a dry ethereal solution of 2.5 g of diazomethane, and the resulting mixture was set aside at room temperature overnight. The ether was distilled off under reduced pressure, the residue was dissolved, with cooling, in 60 ml of absolute methanol, 0.8 g of silver oxide was added, and the mixture was boiled in a water bath for eight hours. Vigorous evolution of nitrogen began at 40°. The mixture was treated with charcoal and filtered, the methanol was distilled off under reduced pressure, and the liquid reaction product was boiled with 17 ml of 40% caustic potash and 17 ml of methanol for four hours. The dark-colored solution was treated with charcoal and filtered, the methanol was distilled off under reduced pressure, the alkaline solution was acidified with hydrochloric acid, and the mixture was extracted with ether. The residue remaining after removal of ether was dissolved in a small amount of acetone, from which it slowly crystallized out, yielding 0.4 g of crystals, m.p. 168-173°, which after recrystallization from acetone melted at 175-177° and showed no depression in admixture with trans-2-carboxy-2-methylcyclohexaneacetic acid (XXXIX). From the acetone mother liquor, after addition of an equal volume of petroleum ether, 0.5 g of a nonhomogeneous crystalline product, m.p. 125-140° was obtained. Two recrystallizations from a mixture of acetone and petroleum ether (1:1) yielded 0.2 g of pure cis-2-carboxy-2-methylcyclohexaneacetic acid (XX), m.p. 164-165°.

Anilides of cis-Monoesters, and their Reactions

1. Anilide of the carboxy^2-Monomethyl Ester of cis-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (XXIV). A solution of 0.5 g of aniline in 5 ml of absolute ether was added slowly to a cooled (to − 5°) and stirred solution of 0.5 g of the cis-acid chloride (XIV) in 5 ml of absolute ether. The mixture was allowed to stand for 30 minutes at 0°. Water was then added, and the ether layer was separated, washed successively with 5% hydrochloric acid, 10% sodium carbonate, and water, and then dried. After removal of ether, an oily substance remained, and this solidified when treated with petroleum ether (0.60 g, m.p. 82-87°). After recrystallization from a mixture of diethyl

ether and petroleum ether, the anilide melted at 91-93°.

Found %: C 70.57, 70.58; H 6.96, 7.14; N 5.29, 5.11
$C_{16}H_{19}O_3N$. Calculated %: C 70.30; H 7.00; N 5.30

2. Anilide of the carboxy[1]-Monomethyl Ester of cis-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (XXV). The procedure of the preceding experiment applied to 0.5 g of the cis-acid chloride (XVIII) and 0.5 g of aniline in ether yielded 0.50 g of a crystalline product, which melted after crystallization from a mixture of diethyl ether and petroleum ether at 104-105° and which corresponded in analysis to the cis-anilide (XXV).

Found %: C 70.54, 70.50; H 7.34, 7.10; N 5.12, 5.35
$C_{16}H_{19}O_3N$. Calculated %: C 70.30; H 7.00; N 5.30

3. Phenylimide of 1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (XXIII). a) Finely ground phosphorus pentachloride (0.6 g) was added to a solution of 0.4 g of the monoester (VII) (m.p. 120-121°) in 10 ml of absolute ether, and the mixture was heated until solution was complete. The solution was stirred at 20-25°, and 4 g of aniline was slowly added. The mixture was boiled for 30 minutes. Water was added, and the separated ether layer was carefully washed, successively with 10% hydrochloric acid, 5% sodium carbonate, and water. The ether was distilled off, and the yellow crystalline residue was washed on the filter with a mixture of diethyl ether and petroleum ether (1:1) (0.35 g of white crystals, m.p. 98-100°). In order to purify the product, it was dissolved in ether, and the ether solution, after filtration to remove undissolved impurities, was evaporated to low bulk, when an equal volume of petroleum ether was added. Needles of m.p. 103-104° separated, and they corresponded in composition to the phenylimide (XXIII).

Found %: C 74.47, 74.29; H 6.20, 6.42; N 5.94, 6.02
$C_{16}H_{15}O_2N$. Calculated %: C 74.66; H 6.26; N 5.80

b) In a similar way, 0.3 g of the liquid cis-monoester (IX) yielded 0.2 g of a crystalline substance, which melted after crystallization from ether at 103-104° and showed no melting-point depression in admixture with the imide (XXIII).

c) A solution of 0.5 g of aniline in 5 ml of ether was added to a stirred solution of 0.5 g of the cis-acid chloride (XIV) in 5 ml of absolute ether. The ether solution was boiled for 30 minutes, and then washed successively with 5% hydrochloric acid, 10% sodium carbonate, and water. The ether was distilled off, and the residue (0.6 g) was recrystallized from a small amount of ether, yielding 0.35 g of the imide (XXIII), m.p. 102-103°.

d) The same imide (XXIII) of m.p. 103-104° was obtained by the same method from the cis-acid chloride (XVIII).

e) A solution of 0.1 g of the cis-anilide (XXIV), m.p. 92-93°, in 4 ml of absolute ether and 0.2 ml of phosphoryl chloride were boiled together for one hour. The ether solution was washed successively with 10% sodium carbonate and water, and then dried. The ether was distilled off, and the residue, after crystallization from a mixture of diethyl ether and petroleum ether (1:1), melted at 102-103° and showed no melting-point depression in admixture with the imide (XXIII).

f) The same procedure applied to the anilide (XXV) yielded a crystalline product of m.p. 102-103°, identical with the imide (XXIII).

4. Phenylimide of 1-Methyl-1,2-cyclohexanedicarboxylic Acid (XXII). Phosphorus pentachloride (1.5 g) was added to an ethereal solution of 1 g of the cis-monoester (XI) (m.p. 69-70°), and the mixture was boiled until solution was practically complete. Aniline (10 ml) was added at 20-25°. The reaction mixture was treated with water, and the separated ether layer was washed successively with 10% hydrochloric acid, 10% sodium carbonate, and water, and then dried with sodium sulfate. The crystalline substance remaining after removal of ether was washed with a mixture of diethyl ether and petroleum ether (1:4), and yielded 0.95 g of a substance of m.p. 105-107°. Crystallization from diethyl ether containing a little petroleum ether gave a pure product, m.p. 109-110°, which corresponded in analysis to the phenylimide (XXII).

Found %: C 74.21, 74.35; H 7.02, 6.89; N 5.65, 5.67
$C_{16}H_{17}O_2N$. Calculated %: C 74.05; H 7.04; N 5.75

The same product was prepared in an analogous way from the isomeric-cis monoester (XIII); it had the same melting point (110-111°). From each of the isomeric acid chlorides (XVII) and (XXI), both with cooling (0°) and with warming (30-35°), the same imide of m.p. 109-110° was obtained by reaction with aniline, and this imide was identical with the above-described phenylimide (XXII).

carboxy[1]-Monomethyl Ester of trans-1-Methyl-4-cyclohexene-1,2-carboxylic Acid (XXVIII). a) The anhydride of trans-1-methyl-4-cyclohexene-1,2-carboxylic acid (XXVI, 3.5 g) was added slowly to a warm solution of 1 g of sodium in 30 ml of absolute methanol and boiled for one hour. The methanol was distilled off under reduced pressure, and the residue was dissolved in 20 ml of water. The solution was treated with charcoal, filtered, and acidified with hydrochloric acid to Congo red. A liquid reaction product separated, and this solidified almost completely after standing. The solid was filtered off, and washed with water and with a mixture of diethyl ether and petroleum ether (1:5) (2.2 g of crystals, m.p. 71-74°). The liquid part, after long standing, yielded a further 0.25 g of crystals, m.p. 70-73°; the total yield was 60%. After crystallization from petroleum ether the trans-monoester (XXVIII) had a constant melting point of 74-75°.

Found %: C 60.64, 60.57; H 7.29, 7.05
$C_{10}H_{14}O_4$. Calculated %: C 60.60; H 7.12

Anilide: Finely ground phosphorus pentachloride (0.75 g) was added to a solution of 0.5 g of the trans-monoester (XXVIII) in 20 ml of absolute ether. The mixture was heated until solution was complete, excess of aniline was added, and the mixture was allowed to stand at room temperature for one hour. Water was added, and the ether layer was separated, washed successively with 10% hydrochloric acid, 10% sodium carbonate solution, and water, and then dried. The ether was distilled off, and the crystalline residue was washed on the filter with a mixture of diethyl ether and petroleum ether (1:4) (0.4 g of crystals, m.p. 125-129°). After crystallization from ether, the trans-anilide (XXXII) was obtained in the form of needles, m.p. 133-134°.

Found %: N 5.15, 5.34
$C_{16}H_{19}O_3N$. Calculated %: N 5.30

b) The dimethyl ester of trans-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (XXVII) (6 g) was added to a solution of 1.7 g of caustic potash in 25 ml of water and 90 ml of methanol, and the mixture was boiled for ten hours. Methanol was distilled off under reduced pressure, and the residual solution was extracted with ether to remove unhydrolyzed diether (1.8 g). The aqueous solution was treated with charcoal and filtered, and then acidified with hydrochloric acid. A liquid hydrolysis product separated, and this partially crystallized on standing. The crystalline product was filtered off and washed with petroleum ether, yielding 2.3 g of the trans-monoester (XXVIII), m.p. 71-75°. The liquid part, after extraction with ether, removal of ether, and treatment of the residue with petroleum ether, yielded a further 0.15 g of the crystalline trans-monoester (XXVIII), m.p. 71-74° (total yield 63%). After crystallization from petroleum ether, the product melted at 73-74°.

carboxy[1]-Monomethyl Ester of trans-1-Methyl-1,2-cyclohexanedicarboxylic Acid (XXIX). a) A solution of the carboxy[1]-monomethyl ester of trans-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (XXVIII, 1.5 g), m.p. 73-74°, in 15 ml of absolute methanol was treated with hydrogen in presence of a Pd catalyst. One molecule of hydrogen (185 ml at 750 mm and 16°) was absorbed. When the solvent was distilled off, the hydrogenation product was caused to solidify by treatment with petroleum ether, and was recrystallized from a mixture of benzene and petroleum ether (1:5), yielding 1.35 g of the trans-monoester XXIX, m.p. 92-93°, which is in accord with data in the literature [2].

Found %: C 59.73; 59.74; H 7.92; 8.02
$C_{10}H_{16}O_4$. Calculated %: C 60.0 H 8.05

Anilide: The trans-monoester XXIX (0.3 g) was treated in the usual way with phosphorus pentachloride and aniline in ether solution, and 0.2 g of a crystalline product was obtained, which melted, after recrystallization from 40% methanol, at 103-105° and corresponded in analysis to the normal trans-anilide (XXXIII).

Found %: C 69.89; H 7.87; N 5.23
$C_{16}H_{21}O_3N$. Calculated %: C 69.80; H 7.70; N 5.08

b) The anhydride of trans-1-methyl-4-cyclohexene-1,2-dicarboxylic acid (XXVI, 1.3 g) was added slowly to a solution of 0.35 g of sodium in 12 ml of absolute methanol, and the solution was boiled in a water bath for 30 minutes. Water (10 ml) was added, methanol was distilled off under reduced pressure, and the aqueous solution was treated with charcoal, filtered, and acidified with hydrochloric acid. When the mixture, was cooled and allowed to stand, the liquid reaction product completely crystallized; it was filtered off, and washed with water and with petroleum ether (1.2 g, i.e., 77%; m.p. 86-92°). After crystallization from a mixture of benzene and petroleum ether, it melted at 91-93° and was found to be identical with the trans-monoester XXIX obtained previously (above).

c) The dimethyl ester of trans-1-methyl-1,2-cyclohexanedicarboxylic acid (XXXI, 9.4 g) was added to a solution of 2.8 g of caustic potash in 42 ml of water and 115 ml of methanol, and the mixture was boiled for ten hours. Methanol was removed under reduced pressure, and the residue was extracted with ether to remove unhydrolyzed

diester (2.1 g), treated with charcoal and filtered, and acidified. The crystalline product was filtered off and washed with water and with petroleum ether (5.1 g, i.e., 75% on the amount of trans-diester hydrolyzed, of the trans-monoester XXIX; m.p. 85-90°). After crystallization from a mixture of benzene and petroleum ether, the pure trans-monoester melted at 92-93.5°.

Reaction of the Anhydride of trans-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (XXVI) with Methanol. A solution of 4 g of the trans-anhydride XXVI in 15 ml of absolute methanol was boiled in a water bath for four hours. After removal of methanol under reduced pressure, a viscous noncrystallizing reaction product was obtained, and this was dissolved in a small amount of warm petroleum ether and set aside at room temperature overnight with addition of seeding crystals of the trans-monoester XXVIII. Crystals (0.15 g) of m.p. 73-75° appeared; they were identical with the trans-monoester XXVIII. From the mother liquor, on long standing (10-15 days) a nonhomogeneous crystalline product (3.2 g, m.p. 43-55°) gradually separated. Fractional crystallization from petroleum ether yielded 0.2 g of the pure trans-monoester XXVIII and 1.2 g of another substance, which crystallized in the form of fine needles, m.p. 56-58°, and corresponded in alaysis to the isomeric trans-monoester XXXIV.

Found %: C 60.72; 60.76; H 7.17; 7.28
$C_{10}H_{14}O_4$. Calculated %: C 60.6 H 7.12

Anilide: The anilide of the trans-monoester XXXIV was obtained in the usual way. It melted, after crystallization from ether, at 112-114°, and it corresponded in composition to the normal trans-anilide (XXXV).

Found %: N 5.02; 5.30
$C_{16}H_{19}O_3N$. Calculated %: N 5.30

When the trans-monoester XXXIV was hydrogenated in methanol in presence of a Pd catalyst, a saturated liquid trans-monoester was obtained. This was converted into an anilide in the usual way, and the product, crystallized from a mixture of diethyl ether and petroleum ether, melted at 98-99° and corresponded in composition to the normal trans-anilide (XXXVI).

Found %: N 5.14; 5.07
$C_{16}H_{21}O_3N$. Calculated %: N 5.08

Acid Chloride of the carboxy[1]-Monomethyl Ester of trans-1-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (XXXVII). Oxalyl chloride (10 ml) was added to a solution of 8.5 g of the trans-monoester XXVIII in 70 ml of absolute benzene. The solution was set aside at room temperature overnight and then heated at 40° for 30 minutes. Benzene was distilled off, and the residue was a vacuum-distilled, yielding 8.7 g of the trans-acid chloride XXXVII, b.p. 104-105° (4 mm); n_D^{22} 1.4880.

Found %: Cl 16.55; 16.61
$C_{10}H_{13}O_3Cl$. Calculated %: Cl 16.35

With aniline in ether solution the acid chloride XXXVII gave the pure trans-anilide (XXXII), m.p. 133-134°.

Acid Chloride of the carboxy[1]-Monomethyl Ester of trans-1-Methyl-1,2-cyclohexanedicarboxylic Acid (XL). Oxalyl chloride (7 ml) was added to a solution of 6.6 g of the trans-monoester XXIX in 60 ml of absolute benzene, and the solution was set aside at room temperature for two hours. The solvent was distilled off, and the residue was vacuum-distilled, yielding 6.9 g of the trans-acid chloride XL, b.p. 96-97° (1.5 mm); n_D^{22} 1.4770.

Found %: Cl 16.35; 16.26
$C_{10}H_{15}O_3Cl$. Calculated %: Cl 16.17

With aniline in ether solution it gave the normal anilide, m.p. 104-105°, identical with the trans-anilide XXXIII.

trans-6-Carboxy-6-methyl-3-cyclohexene-1-acetic Acid (XXXVIII). A solution of 3 g of the trans-acid chloride XXXVII in 20 ml of absolute ether was added slowly to a cooled stirred dry ethereal solution of 2.5 g of diazomethane, and the mixture was set aside at room temperature overnight. Ether was removed under reduced pressure, and the crystalline residue of diazo ketone was dissolved with cooling in 60 ml of absolute methanol. Freshly prepared silver oxide (0.8 g) was added, and the mixture was boiled for eight hours. The solution was treated with charcoal and filtered, methanol was removed under reduced pressure, and the liquid residue was hydrolyzed with 15 ml of 40% caustic potash and 10 ml of methanol at the boil for four hours. The solution was treated with charcoal and filtered, methanol was distilled off under reduced pressure, and the aqueous solution was acidified with hydrochloric acid. The crystalline product was filtered off and washed carefully with water (2.35 g, i.e., 85.5%; m.p. 193-197°). Two crystallizations from acetone yielded pure trans-6-carboxy-6-methyl-3-cyclohexene-1-acetic acid (XXXVIII) having a constant melting point of 205-206°.

Found %: C 60.73; 60.75; H 7.10; 7.23

$C_{10}H_{14}O_4$. Calculated %: C 60.6 H 7.12

trans-2-Carboxy-2-methlcyclohexaneacetic Acid (XXXIX). a) An ethereal solution of 2.0 g of the trans-acid chloride XL was added slowly to a cooled dry ethereal solution of diazomethane prepared from 10 g of methylnitrosourea , and the mixture was set aside at room temperature overnight. Ether was removed under reduced pressure, and the crystalline diazo ketone (m.p. 42-44°) was dissolved in 40 ml of cold absolute methanol; 0.6 g of silver oxide was added, and the mixture was boiled for six hours. Methanol was distilled off, and the liquid product was hydrolyzed with 10 ml of 40% caustic potash and 5 ml of methanol at the boil for five hours. The solution was filtered and acidified with hydrochloric acid. A semisolid product was precipitated, and this was filtered off and washed with water and a mixture of acetone and petroleum ether (1:5). The product, 0.8 g of a crystalline acid, m.p. 175-177°, was pure trans-2-carboxy-2-methylcyclohexaneacetic acid (XXXIX) [2].

Found %: C 60.07; 60.32; H 8.35; 8.25

$C_{10}H_{16}O_4$. Calculated %: C 60.0 H 8.06

The aqueous mother liquor and washings were evaporated to dryness under reduced pressure and extracted with acetone. Removal of acetone and treatment of the residue with petroleum ether yielded a further 0.2 g of the trans-acid, m.p. 165-175°, and this, after crystallization from a mixture of acetone and petroleum ether (1:2) melted at 176-177°. The total yield was 60%.

b) A solution of 0.8 g of trans-6-carboxy-6-methyl-3-cyclohexene-1-acetic acid (XXXVIII) in 20 ml of absolute methanol was hydrogenated over a Pd catalyst, and one molecule of hydrogen was absorbed. The solvent was distilled off, and the hydrogenation product was washed on the filter with a mixture of diethyl ether and petroleum ether (1:2), and yielded 0.75 g of pure trans-2-carboxy-2-methylcyclohexaneacetic acid (XXXIX), m.p. 175-177°, identical with the product obtained in the first experiment.

SUMMARY

1. The crystalline cis-monoester VII and the liquid cis-monoester IX have been prepared from the cis-anhydride VI, the cis-dicarboxylic acid VIII, and the ester of this acid (X). By hydrogenation of these monoesters the corresponding saturated cis-monoesters XI and XIII have been prepared, and the structures of these have been proved by converting them into the known cis-carboxymethyl cyclohexaneacetic acids XVI and XX.

2. It has been found that, when the unsaturated cis-monoesters VII and IX and their acid chlorides XIV and XVIII react with aniline at 30°, the same product, the phenylimide XXIII, is obtained in all cases. Only under very mild reaction conditions (0°) was it possible to isolate the corresponding cis-anilides (XXIV and XXV), readily converted when heated with phosphoryl chloride into the phenylimide XXIII.

3. In the case of the cis-acid chlorides XVII and XXI, lengthening of the carbon chain occurs with partial conversion to the corresponding trans-acids XXXVIII and XXXIX. The secondary carboxy group enters into the Arndt-Eistert reaction considerably more readily than the tertiary carboxyl group.

4. The trans-monoester XXVIII, hydrogenation of which gives the saturated trans-monoester XXIX, was prepared in satisfactory yield from the trans-anhydride XXVI and the trans-diester XXVII.

5. The monoester and acid chlorides of the trans series readily give stable anilides, and they enter the Arndt-Eistert reaction considerably more readily than do the monoesters of the cis series.

Received October 13, 1952 Institute of Organic Chemistry of the USSR Academy of Sciences

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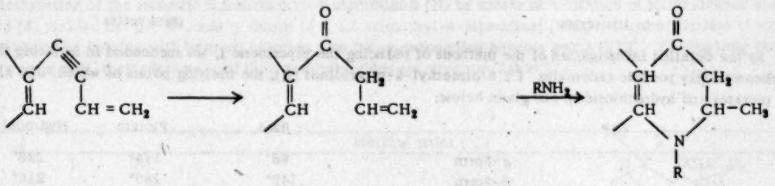
HETEROCYCLIC COMPOUNDS

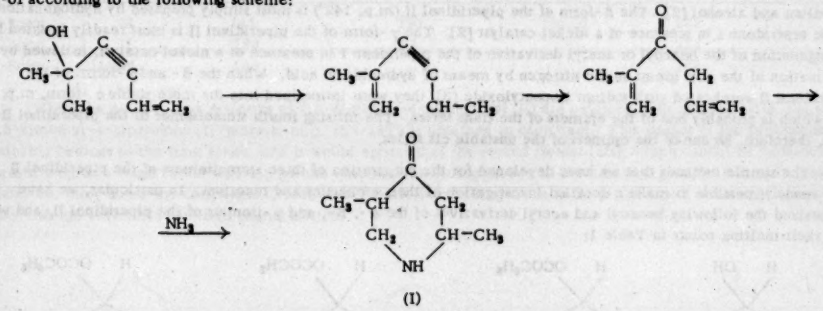
COMMUNICATION XXIX. STEREOISOMERISM OF 2,5-DIMETHYL-4-PIPERIDINOL, 1,2,5-TRIMETHYL-4-PIPERIDINOL, AND THEIR DERIVATIVES*

I. N. Nazarov, D. V. Sokolov, and V. N. Rakcheeva

Some years ago, Nazarov and his coworkers developed a new simple method for the preparation of various 4-piperidones by the use of acetylene [1]:



The discovery of this method, which made a very great variety of 4-piperidones readily accessible, enabled investigations into the synthesis of compounds of the piperidine series to be greatly extended and has led to the discovery of very valuable new medicinals having a sedative action (substitutes for morphine). The physiological activity of these compounds is generally greatly dependent not only on the number, disposition, and nature of the substituents in the piperidine ring, but also on their spatial arrangement. Investigations into the stereochemistry of piperidine derivatives are, therefore, not only of theoretical, but also of practical interest; and their importance is increased by the fact that this field has received very little study. As our starting substance for these stereochemical investigations we selected 2,5-dimethyl-4-piperidone (I), which is readily prepared from 2-methyl-5-hexen-3-yn-2-ol according to the following scheme:



(I)

The piperidone I, having two asymmetric carbon atoms, may exist in two racemic forms, cis and trans:

cis form trans form

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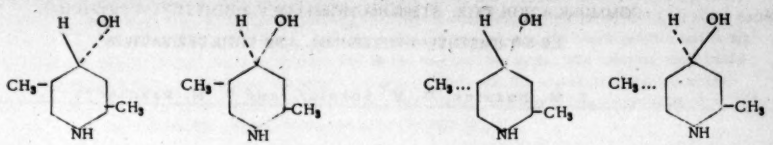
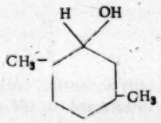
All attempts, however, to separate these piperidones, or their derivatives, have resulted in the isolation of only one form, probably the trans form, of the piperidone I; it was not found possible to isolate the other isomer. When the carbonyl group of the piperidone I was reduced, 2,5-dimethyl-4-piperidinol (II) was formed, and this now has three asymmetric carbon atoms and may exist in four racemic forms corresponding to the following spatial dispositions of substituents:



cis series trans series

By the detailed investigation of the methods of reducing the piperidone I, we succeeded in isolating three of four theoretically possible racemates f 2,5-dimethyl-4-piperidinol (II), the melting points of which, and also of their picrates and hydrochlorides, are given below:

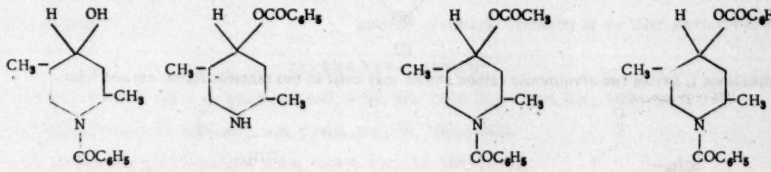


(II)

	Base	Picrate	Hydrochloride
α-Form	98°	174°	223°
β-Form	142°	180°	210°
γ-Form	87°	oil	188°

The α-form of the piperidinol II (m.p. 98°) is most readily obtained by reduction of the piperidone I by means of sodium and alcohol [2]. The β-form of the piperidinol II (m.p. 142°) is most simply prepared by hydrogenation of the piperidone I in presence of a nickel catalyst [2]. The γ-form of the piperidinol II is most readily isolated by hydrogenation of the benzoyl or acetyl derivative of the piperidone I in presence of a nickel catalyst, followed by elimination of the acyl group on the nitrogen by means of hydrochloric acid. When the β- and γ-forms of the piperidinol II wereheated with sodium isopentyloxide [3], they were isomerized into the more stable α-form, m.p. 98°, which is probably one of the epimers of the trans series. The missing fourth stereoisomer of the piperidinol II must, therefore, be one of the epimers of the unstable cis series.

The simple methods that we have developed for the preparation of three stereoisomers of the piperidinol II have made it possible to make a detailed investigation of their properties and reactions. In particular, we have synthesized the following benzoyl and acetyl derivatives of the α-, β-, and γ-isomers of the piperidinol II, and we give their melting points in Table 1:



(III) (IV) (V) (VI)

TABLE 1

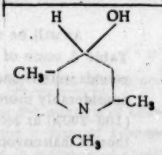
	α-Form	β-Form	γ-Form
III	137°	135°	160°
IV	Picrate 195°; Hydrochloride 266°	Picrate 236°; Hydrochloride 168°	Picrate 174°; Hydrochloride 254°
V	Oil	126°	93°
VI	93°	93°	118°

Although the benzoyl derivatives of the α- and β-forms of III and VI have identical melting points, these are greatly depressed in mixture tests, and there can be no doubt that they are different substances.

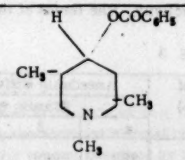
The benzoyl derivatives III were readily prepared in high yield (about 90%) by the action of benzoyl chloride on the piperidinols II in presence of alkali. The benzoic esters IV were prepared by heating benzoyl chloride with the hydrochlorides of the piperidinols II at 140-150°. The mixed diacyl derivatives V were prepared by acetylation of the benzoyl derivatives III with acetic anhydride, and the dibenzoyl derivatives VI were obtained by benzoylation of the monobenzoyl derivatives III or IV with benzoyl chloride.

Methylation of the isomeric 2,5-dimethyl-4-piperidinols (II) by means of a mixture of formaldehyde and formic acid [4] yielded the α-, β-, and γ-forms of 1,2,5-trimethyl-4-piperidinol (VII), the hydrochlorides of which were converted by heating with benzoyl chloride into the corresponding benzoic esters (VIII). The melting points of these compounds, their picrates, and their hydrochlorides are given in Table 2.

TABLE 2



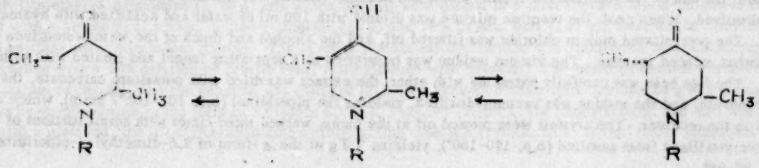
(VII)



(VIII)

	Melting point (°C)					
	Base	Picrate	Hydrochloride	Base	Picrate	Hydrochloride
α-Form	73	143	196	Liquid	200	202
β-Form	78	183	Oil		218	Oil
γ-Form	Liquid	168			182	179

When the α-, β-, and γ-forms of 2,5-dimethyl-4-piperidinol (II) are oxidized with chromic acid, the same 2,5-dimethyl-4-piperidone (I) (picrate, m.p. 168-169°) is obtained in each case. This isomer of the piperidone I probably belongs to the trans series, and it would appear that the second isomer (cis), which cannot be isolated, is formed only as a stage in the reaction (of the reduction or hydrogenation of the carbonyl group). It is quite possible, therefore, that, under the conditions of reduction or catalytic hydrogenation, the piperidone I and its N-derivatives may undergo reversible cis-trans isomerization:

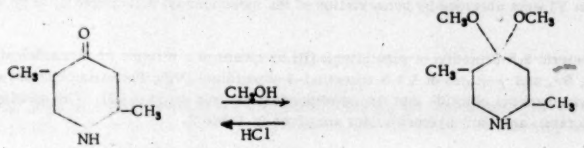


Similar transformations may occur also under the action of organometallic compounds (RMgX, RLi), and also in the condensation of 4-piperidones with acetylene in presence of caustic potash, sodamide, or sodium in liquid ammonia.

In a careful investigation of the conditions required for the formation of picrates of the piperidone I, we established that a component ratio of 1:1 led to the formation of the normal picrate, m.p. 169° (large yellow rods), and that in presence of an excess of the piperidone I a picrate of m.p. 138° (yellow needles) was formed, which contained one molecule of picric acid for each two molecules of the piperidone. The picrates are interconvertible:

$$\text{Picrate, m.p. 169°} \xrightarrow[\text{picric acid}]{\text{piperidone I}} \text{Picrate, m.p. 138°}$$

When the piperidone I was treated with a hot methanolic solution of an equimolecular proportion of picric acid, together with the ordinary picrate (m.p. 169°), the picrate of the dimethyl ketal (IX), m.p. 122-123°, was obtained also. Decomposition of this picrate with an aqueous solution of potassium carbonate yielded the free dimethyl ketal (IX), and this was hydrolyzed with dilute hydrochloric acid with formation of methanol and the piperidone I:



The hydrochlorides of the α-, β-, and γ-forms of the benzoic esters IV and VIII were tested for their anesthetic activity. The results of these tests are given in Table 3.

TABLE 3

Conc. of soln. (%)	Anesthetic activity in Renier units (average values)*						Novocaine
	Benzoic esters IV			Benzoic esters VIII			
	α	β	γ	α	β	γ	
0.25	223	269	569	343	409	295	109
0.5	474	492	815	544	693	588	181
1.0	629	376	924	721	1089	700	255
2.0	594	861	1106	933	812	1010	309

As will be seen from Table 3, some of the compounds were found to be considerably more active (100-200%) as local anesthetics than novocaine. However, owing to their high toxicity and irritative action, they are not of practical importance.

* The tests were carried out in the Pharmacology Department of the V. M. Molotov Kazakhstan Medical Institute by Gordin, Samarina, and Chebekova.

EXPERIMENTAL

The 2,5-dimethyl-4-piperidone (I) used in this work was prepared by the previously described method and had the following constants: b.p. 78° (7 mm); n_D^{20} 1.4660.

Reduction of 2,5-Dimethyl-4-piperidone with Sodium in Alcoholic Solution (α-Form of 2,5-Dimethyl-4-piperidinol, m.p. 97-98°)

A solution of 12.7 g of 2,5-dimethyl-4-piperidone (I) in 350 ml of absolute alcohol was prepared in a flask fitted with mechanical stirrer, and it was stirred continuously while 35 g of sodium was added in small pieces. Toward the end of the reaction the liquid, which had become viscous, was warmed until the whole of the sodium had dissolved. When cool, the reaction mixture was diluted with 100 ml of water and acidified with hydrochloric acid. The precipitated sodium chloride was filtered off, and the alcohol and much of the water were driven off under somewhat reduced pressure. The viscous residue was transferred to a separating funnel and treated with solid caustic soda. The free base was carefully extracted with ether, the extract was dried with potassium carbonate, the ether was removed, and the residue was vacuum-distilled, yielding the piperidinol (b.p. 101-102°/8mm), which crystallized in the receiver. The crystals were pressed off at the pump, washed three times with small portions of ether, and recrystallized from gasoline (b.p. 120-150°), yielding 7.3 g of the α-form of 2,5-dimethyl-4-piperidinol (II), m.p. 97-98°.

Found %: N 10.81; 10.90

$C_7H_{15}ON$. Calculated %: N 10.85

The picrate was prepared by dissolving 0.5 g of the piperidinol in 30 ml of a saturated methanolic solution of picric acid; it was obtained in the form of rods, m.p. 173-174° (from methanol).

Found %: N 15.77; 15.80

$C_{19}H_{18}O_8N_4$. Calculated %: N 15.64

The hydrochloride was prepared by the action of hydrogen chloride on the piperidinol in alcoholic solution, followed by precipitation with ether; it formed crystals of m.p. 222-223°.

From the ether mother liquors, containing a mixture of noncrystallizing piperidinols, after removal of ether and benzoylation with benzoyl chloride in presence of alkali in the cold, about 1 g of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 160°) was obtained. It showed no melting-point depression with anauthentic sample (see below).

Hydrogenation of 2,5-Dimethyl-4-piperidone in Presence of a Nickel Catalyst (β-Form of 2,5-Dimethyl-4-piperidinol, m.p. 142°

A solution of 20.7 g of the piperidone I in 100 ml of alcohol was treated with hydrogen in presence of 1.5 g of Raney nickel and 0.5 ml of 20% caustic soda. After 20 hours' shaking, 4.1 liters of hydrogen had been absorbed, against 4.3 liters required by theory. The catalyst was filtered off, alcohol was distilled off under somewhat reduced pressure until a dry crystalline residue was obtained, and the residue was washed with ether and recrystallized from gasoline (b.p. 80-100°), yielding 4.1 g of the β-form of 2,5-dimethyl-4-piperidinol (II), m.p. 141-142°, in the form of light scalelike leaves.

Found %: N 10.76; 10.90
$C_7H_{15}ON$. Calculated %: N 10.85

The picrate was prepared by dissolving the piperidinol in a saturated methanolic solution of picric acid. It formed polyhedral prisms, m.p. 179-180° (from methanol). In admixture with the above-described picrate of the α-form (m.p. 173-174°) it melted at 142-146°.

Found %: N 15.90; 15.80
$C_{13}H_{18}O_8N_4$. Calculated %: N 15.64

The hydrochloride formed crystals of m.p. 209-210° (reprecipitated from alcohol).

From the mixture of isomeric piperidinols (16.4 g) remaining after separation of the β-form of m.p. 141-142°, 10.5 g of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III) was obtained by the action of benzoyl chloride in the cold in presence of caustic soda. It melted at 159-160°, and the melting point was not depressed by an authentic sample (see below).

Electrolytic Reduction of 2,5-Dimethyl-4-piperidone

Reduction was carried out at a lead cathode (10.5 cm x 11.2 cm) at a current density of 0.029 amp per sq cm at 20° in a 10% solution of ammonium sulfate [3]. The cathode space was separated from the anode by means of a porous pot. The current was switched on, and 20 ml of the piperidone I was added to the cathode department, when evolution of hydrogen stopped. The reduction was discontinued after five hours (theoretically, 2 hours 30 minutes was required). The cathode solution was transferred to a Claisen flask, acidified with hydrochloric acid, and evaporated almost to dryness under reduced pressure. Excess of solid caustic soda was added to the residue, and the liberated base was extracted with several portions of hot gasoline (b.p. 80-100°). When the gasoline solution stood overnight, 2.2 g of crystals were precipitated, and these, after recrystallization, melted at 141-142° and showed no melting-point depression in admixture with the β-form of 2,5-dimethyl-piperidinol obtained in the preceding experiment.

Benzoylation of 2,5-Dimethyl-4-piperidone

2,5-Dimethyl-4-piperidone (I, 30 g) and water (236 ml) were placed in a three-necked round-bottomed flask provided with a mechanical stirrer. Benzoyl chloride (50 g) and 15% caustic soda (100 ml) were added alternately in small portions under continuous stirring. The layer of viscous oil that formed was transferred to a separating funnel, washed with a 50% solution of caustic soda, and extracted with benzene. The benzene extract was dried with potassium carbonate, and the benzene was distilled off. Two vacuum distillations yielded 50 g of 1-benzoyl-2,5-dimethyl-4-piperidone in the form of a viscous oil, b.p. 192-193° (5 mm). On long standing, and also when rubbed with a glass rod, the oil crystallized completely, giving colorless crystals, m.p. 64-65° (from petroleum ether).

Found %: N 6.04; 6.03
$C_{14}H_{17}O_2N$. Calculated %: N 6.06

A solution of 0.47 g of 1-benzoyl-2,5-dimethyl-4-piperidone was mixed with a solution of 0.4 g of 2,4-dinitrophenylhydrazine and 1.4 ml of concentrated hydrochloric acid in 80 ml of alcohol. The mixture was heated for ten minutes in a water bath and then set aside for five days, when 0.35 g of the 2,4-dinitrophenylhydrazone was obtained (m.p. 211-212°, from a mixture of chloroform and alcohol).

Found %: N 17.09; 17.08

$C_{20}H_{21}O_6N_3$. Calculated %: N 17.00

Hydrogenation of 1-Benzoyl-2,5-dimethyl-4-piperidone

1-Benzoyl-2,5-dimethyl-4-piperidone (21.4 g, m.p. 64-65°) was hydrogenated as a solution in 120 ml of alcohol in presence of 0.5 ml of 20% caustic soda and 1.5 g of Raney nickel. The calculated amount of hydrogen (2500 ml) was absorbed when the flask had been shaken for six hours. The catalyst was filtered off, and the alkali was neutralized with a few drops of hydrochloric acid. Alcohol was then removed under reduced pressure, and the residue remaining in the flask crystallized completely.

Three further similar experiments were carried out, and in this way altogether 120 g of a crystalline mixture of isomers of 1-benzoyl-2,5-dimethyl-4-piperidinol (III) was obtained. From this mixture, by fractional crystallization from benzene, 47 g of the pure γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol, m.p. 159-160°, was obtained.

Found %: N 6.02; 6.09

$C_{14}H_{19}O_2N$. Calculated %: N 6.01

The phenylurethan melted at 178-179° (from gasoline).

Found %: N 8.08; 8.09

$C_{21}H_{24}O_3N_2$. Calculated %: N 7.96

The benzene mother liquor was evaporated down, and gasoline (b.p. 80-100°) was added, resulting in the separation of a further 30 g of crystals, m.p. 88-95°, which consisted mainly of a mixture of the α- and β-forms of 1-benzoyl-2,5-dimethyl-4-piperidinol.

Found %: N 6.05; 6.04

$C_{14}H_{19}O_2N$. Calculated %: N 6.01

Hydrolysis of 1-Benzoyl-2,5-dimethyl-4-piperidinol (γ-Form of 2,5-Dimethyl-4-piperidinol, m.p. 87°

A mixture of 10 g of the pure γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 159-160°) and 100 ml of 18% hydrochloric acid was heated in a boiling water bath for 35 hours. The benzoic acid formed was filtered off, and the filtrate was evaporated to dryness and then treated with a 50% solution of caustic soda. The free base was extracted with ether, dried with potassium carbonate, and vacuum-distilled, yielding 4 g of the γ-form of 2,5-dimethyl-4-piperidinol (II), b.p. 82-84°/2 mm, which completely crystallized in the receiver. It melted, after two crystallizations from gasoline, at 86-87°.

Found %: N 10.71; 10.72

$C_7H_{15}ON$. Calculated %: N 10.85

The picrate formed a thick noncrystallizing oil. The hydrochloride was prepared by the action of hydrogen chloride on the piperidinol in methanol solution, followed by precipitation with dry ether (large needles, m.p. 187-188°).

When the mixture of isomers of 1-benzoyl-2,5-dimethyl-4-piperidinol of m.p. 88-95° was hydrolyzed in a similar way, the α- and β-forms of 2,5-dimethyl-4-piperidinol were isolated; they melted respectively at 98° and 142°, undepressed by addition of the above-described samples. The β-form (m.p. 142°) was precipitated directly from ether, and the α-form (m.p. 98°) was then separated from the mother liquors via the hydrochloride. Hence, in the hydrogenation of 1-benzoyl-2,5-dimethyl-4-piperidone in presence of a nickel catalyst, three isomeric forms (α, β, and γ) of 1-benzoyl-2,5-dimethyl-4-piperidinol (III) were formed.

Acetylation of 2,5-Dimethyl-4-piperidone with Acetic Anhydride

Acetic anhydride (36 g) was added with cooling and stirring to 37.2 g of 2,5-dimethyl-4-piperidone, and the solution obtained, which had become warm, was heated in a boiling water bath for 30 minutes. Acetic acid and excess of acetic anhydride were distilled off under reduced pressure, and the residue was washed with 50% caustic soda and extracted with benzene. The benzene extract was dried, and the benzene was removed. Vacuum distillation of the residue yielded 43 g of 1-acetyl-2,5-dimethyl-4-piperidone, b.p. 122-124° (3 mm); n_D^{20} 1.4913; d_4^{20} 1.0792; found MR 45.36; calculated MR 45.52. On standing, the substance solidified completely to crystals of m.p. 56-57° (from petroleum ether).

Found %: N 8.38; 8.31

$C_9H_{15}O_2N$. Calculated %: N 8.28

Acetylation of 2,5-Dimethyl-4-piperidone with Ketene

A current of gaseous ketene, prepared by the pyrolysis of acetone in a porcelain tube at 600-700°, was passed for two hours through a solution of 27.3 g of 2,5-dimethyl-4-piperidone in 50 ml of dioxane contained in a special acetylation apparatus. The acetylation product, after removal of dioxane, was vacuum-fractionated, yielding 34 g of 1-acetyl-2,5-dimethyl-4-piperidone, b.p. 117-118° (2 mm); n_D^{20} 1.4925; d_4^{20} 1.0816; found MR 45.41; calculated MR 45.52. On standing, the substance solidified completely to crystals of m.p. 56-57°, undepressed by the sample obtained in the preceding experiment. The 2,4-dinitrophenylhydrazone melted at 177-179° (from alcohol).

	Found %:	N 20.19; 20.03
$C_{15}H_{19}O_5N_5$.	Calculated %:	N 20.07

Hydrogenation of 1-Acetyl-2,5-dimethyl-4-piperidone

1-Acetyl-2,5-dimethyl-4-piperidone (10.3 g) was hydrogenated as a solution in 90 ml of alcohol in presence of 0.5 ml of 20% caustic soda and 2 g of Raney nickel. The calculated amount of hydrogen (1.68 liters) had been absorbed when the flask had been shaken for two hours. The catalyst was filtered off, the alcohol was driven off, and the residue was dissolved in benzene. The benzene solution was dried with potassium carbonate, and the residue remaining after removal of benzene was vacuum-distilled, yielding 9.4 g of a mixture of isomers of 1-acetyl-2,5-dimethyl-4-piperidinol in the form of a thick syrup, b.p. 135-138° (2 mm). Two further similar experiments were carried out, and altogether 30 g of hydrogenation products was obtained, and from this, on standing, 9 g of crystals of the γ-form of 1-acetyl-2,5-dimethyl-4-piperidinol was obtained in the form of long rods, m.p. 86-87° (from gasoline of b.p. 80-100°).

	Found %:	N 8.13; 8.19
$C_9H_{17}O_2N$.	Calculated %:	N 8.18

The phenylurethan melted at 232-233° (from benzene).

	Found %:	N 9.82; 9.76
$C_{16}H_{22}O_3N_2$.	Calculated %:	N 9.65

Hydrolysis of 1-Acetyl-2,5-dimethyl-4-piperidinol

A mixture of 5.6 g of the above-described γ-form of 1-acetyl-2,5-dimethyl-4-piperidinol (m.p. 86-87°) and 70 ml of 18% hydrochloric acid was heated in a boiling water bath for 30 hours. Acetic and hydrochloric acids were driven off under reduced pressure, and the residue was treated with 50% caustic soda solution. The base was extracted with ether, the ether extract was dried with potassium carbonate, and the residue after removal of ether was crystallized from gasoline (b.p. 80-100°), yielding 3 g of the γ-form of 2,5-dimethyl-4-piperidinol, m.p. 86-87°, undepressed by the substance obtained by the hydrolysis of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol, which is described above.

Isomerization of the β-Form of 2,5-Dimethyl-4-piperidinol

The β-form of 2,5-dimethyl-4-piperidinol (4 g, m.p. 141-142°) was boiled for 43 hours at 180-190° with a solution of sodium isopentyloxide obtained by dissolving 7 g of sodium in 50 ml of isopentyl alcohol. An equal volume of water was added to the hot solution, and the layer of alcohol that separated was washed six times with hydrochloric acid (1:1). The acid extracts were added to the water layer, which was then extracted with ether and evaporated to low bulk. The precipitated sodium chloride was filtered off and washed with hydrochloric acid. The mother liquor was evaporated under reduced pressure to a thick syrup and treated with 50% caustic soda. The base was extracted with ether, and the extract was dried with potassium carbonate. The residue after removal of ether was crystallized three times from gasoline (b.p. 120-150°), yielding 1.2 g of the α-form of 2,5-dimethyl-4-piperidinol, m.p. 96-98°, undepressed by the above-described sample.

Isomerization of the γ-Form of 2,5-Dimethyl-4-piperidinol

The γ-form of 2,5-dimethyl-4-piperidinol (4 g, m.p. 86-87°) was boiled for 46 hours with a solution of sodium isopentyloxide. The reaction product was treated as in the preceding experiment. After removal of ether, the base was vacuum-distilled, and yielded 1.1 g of crude product, b.p. 83-84° at 1.5 mm. Three crystallizations from gasoline yielded 0.4 g of crystals of the α-form of 2,5-dimethyl-4-piperidinol, m.p. 96-97°, undepressed by an authentic sample.

α-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

Benzoyl chloride (2.2 g) was added to a cooled (ice water) solution of 2 g of the α-form of 2,5-dimethyl-4-piperidinol (II) (m.p. 97-98°) in 6 ml of water containing 0.62 g of caustic soda. The mixture was shaken vigorously until the odor of benzoyl chloride disappeared (30 minutes). The lumps that had formed were ground up, washed three times with water, and dried in a vacuum desiccator, yielding 2.6 g of the α-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III), m.p. 136-137° (from a mixture of benzene and gasoline, 7:3).

Found %: N 6.23
$C_{14}H_{19}O_2N$. Calculated %: N 6.05

β-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

Benzoylation of 2 g of the β-form of 2,5-dimethyl-4-piperidinol (II, m.p. 141-142°) by the above-described method yielded 2.65 g of the β-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III), m.p. 134-135° (from a 1:1 mixture of benzene and gasoline).

Found %: N 6.01; 6.09
$C_{14}H_{19}O_2N$. Calculated %: N 6.05

A mixture test with the α-form (m.p. 136-137°) obtained in the preceding experiment showed a depression (m.p. 112-116°).

Benzoic Ester of the α-Form of 2,5-Dimethyl-4-piperidinol

A mixture of 5 g of the hydrochloride of the α-form of 2,5-dimethyl-4-piperidinol (m.p. 222°) and 8 g of freshly distilled benzoyl chloride was heated at 140-150° until hydrogen chloride ceased to be evolved (about one hour). The product was dissolved in water, extracted several times with ether, and treated with sodium carbonate. The liberated base was dissolved in ether, and the ether solution was dried with sodium sulfate. Removal of ether followed by vacuum distillation of the residue yielded 2.2 g of the benzoic ester of the α-form of 2,5-dimethyl-4-piperidinol (IV) in the form of a slightly yellowish liquid, b.p. 164-165° (6 mm); n_D^{20} 1.5240; d_4^{20} 1.0623; found MR 67.12; calculated MR 66.30.

Found %: N 6.16
$C_{14}H_{19}O_2N$. Calculated %: N 6.05

The picrate was obtained by mixing the benzoic ester with a saturated solution of picric acid in methanol: fine needles, m.p. 194-195° (from methanol).

Found %: N 12.5; 12.4
$C_{20}H_{22}O_9N_4$. Calculated %: N 12.12

The hydrochloride was obtained by precipitation from alcohol with ether: minute needles, m.p. 265-266°, moderately soluble in water, readily soluble in alcohol.

Benzoic Ester of the β-Form of 2,5-Dimethyl-4-piperidinol

A mixture of 3 g of the hydrochloride of the β-form of 2,5-dimethyl-4-piperidinol (m.p. 209-210°) and 3.2 g of benzoyl chloride was heated at 140-150°, as described above. The usual treatment yielded 2.5 g of the benzoic ester of the β-form of 2,5-dimethyl-4-piperidinol (IV) in the form of a yellowish liquid, b.p. 166° (7 mm); n_D^{20} 1.5250; d_4^{20} 1.0860; found MR 66.76; calculated MR 66.30.

Found %: N 6.26
$C_{14}H_{19}O_2N$. Calculated %: N 6.05

Picrate: long coarse needles, m.p. 235-236° (from methanol).

Found %: N 12.47; 12.29
$C_{20}H_{22}O_9N_4$. Calculated %: N 12.42

Hydrochloride: fine, matted needles, m.p. 167-168.5° (from a mixture of alcohol and ether), readily soluble in water and alcohol.

Benzoic Ester of the γ-Form of 2,5-Dimethyl-4-piperidinol

A mixture of 10 g of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 159-160°) and 10 g of freshly distilled benzoyl chloride was heated at 170° until the evolution of hydrogen chloride ceased. A current of dry hydrogen chloride was then passed through the reaction mixture at the same temperature for two hours. The

precipitated hydrochloride was washed with benzene and dissolved in a small amount of water. The hydrochloride was decomposed with a saturated solution of sodium carbonate, and the liberated base was extracted with ether. The ether extract was dried with sodium sulfate, and the ether was driven off. Vacuum distillation of the residue yielded 5.5 g of the benzoic ester of the γ-form of 2,5-dimethyl-4-piperidinol (IV) in the form of a colorless liquid, b.p. 125-126° (1 mm); n_D^{20} 1.5265; d_4^{20} 1.0633; found MR 67.3; calculated MR 66.3.

Found %: N 5.83

$C_{14}H_{19}O_2N$. Calculated %: N 6.05

Picrate: fine convex rosettes, m.p. 173-174.5° (from methanol).

Found %: N 12.13; 12.16

$C_{20}H_{22}O_9N_4$. Calculated %: N 12.12

Hydrochloride: fine needles, m.p. 253-254° (precipitation from alcohol with ether), soluble in water and alcohol.

Benzoic Ester of the α-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

A mixture of 2 g of the benzoic ester of the α-form of 2,5-dimethyl-4-piperidinol (IV), 5 ml of 10% caustic soda, and 1.8 g of freshly distilled benzoyl chloride was cooled with ice water and shaken until the odor of benzoyl chloride disappeared. The thick mass was washed by grinding it with a 10% sodium carbonate solution and then with water, and it was dried in a vacuum desiccator. Three crystallizations from gasoline (b.p. 80-100°) yielded 2 g of the benzoic ester of the α-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (VI) in the form of large rods, m.p. 92-93°.

Found %: N 4.14

$C_{21}H_{23}O_2N$. Calculated %: N 4.15

Benzoic Ester of the β-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

From 3 g of the benzoic ester of the β-form of 2,5-dimethyl-4-piperidinol (IV), the above-described procedure yielded 4.2 g of the benzoic ester of the β-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (VI) in the form of long wide plates, m.p. 92-93° (from gasoline).

Found %: N 4.13

$C_{21}H_{23}O_2N$. Calculated %: N 4.15

Benzoic Ester of the γ-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

A mixture of 3 g of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 159-160°) and 5 g of benzoyl chloride was boiled in benzene solution for 24 hours. The residue remaining after removal of benzene under reduced pressure was crystallized from a mixture of benzene and gasoline. The first crop consisted of 0.5 g of the starting material, m.p. 159-160°. After some evaporation, a precipitate of 2.5 g of the benzoic ester of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (VI), m.p. 117-118° (from gasoline/benzene 7:3), was obtained.

Found %: N 4.13; 4.04

$C_{21}H_{23}O_2N$. Calculated %: N 4.15

Acetic Ester of the α-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

A mixture of 2 g of the α-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 136-137°) and 4 g of acetic anhydride containing one drop of concentrated sulfuric acid was heated at 60° for 7 hours 30 minutes. The excess of acetic anhydride was distilled off under reduced pressure, and the product was washed with a saturated sodium carbonate solution and extracted with ether. The ether extract was dried with calcined sodium sulfate. Vacuum fractionation yielded 2.5 g of the acetic ester of the α-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (V) in the form of a viscous oil, b.p. 187-189° (2 mm); n_D^{20} 1.5290.

Found %: N 5.13

$C_{16}H_{21}O_2N$. Calculated %: N 5.09

Acetic Ester of the β-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

Acetylation of 1.3 g of the β-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 134-135°) by the above-described method yielded 1.4 g of the acetic ester of the β-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (V), m.p. 125-126° (from gasoline).

Found %: N 5.24

$C_{16}H_{21}O_2N$. Calculated %: N 5.09

Acetic Ester of the γ-Form of 1-Benzoyl-2,5-dimethyl-4-piperidinol

Acetylation of 5 g of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (III, m.p. 159-160°) with 10 g of acetic anhydride by the method described above yielded 5 g of the acetic ester of the γ-form of 1-benzoyl-2,5-dimethyl-4-piperidinol (V), m.p. 92.5-93° (from gasoline).

Found %: N 5.07, 5.26

$C_{16}H_{21}O_3N$ Calculated %: N 5.09

α-Form of 1,2,5-Trimethyl-4-piperidinol

A mixture of 3.8 g of 32% formaldehyde, 2.2 g of 90% formic acid, and 5 g of the α-form of 2,5-dimethyl-4-piperidinol (II, m.p. 97-98°) was boiled under reflux in a water bath until evolution of carbon dioxide ceased (6 hours 20 minutes). The cooled solution was treated with solid caustic soda, and the base was extracted with ether. The ether extract was dried with calcined potassium carbonate. Vacuum fractionation yielded 4.7 g of the α-form of 1,2,5-trimethyl-4-piperidinol (VII), b.p. 87-89° (4 mm); n_D^{20} 1.4730; d_4^{20} 0.9541; Found MR 42.13; Calculated MR 42.41. This substance is rather viscous liquid; it crystallizes completely on standing (oblong leaves, m.p. 72-73°).

Found %: N 9.74

$C_9H_{17}ON$. Calculated %: N 9.78

Picrate: fine needles grouped together in starlike clusters, m.p. 142-143° (from methanol). Hydrochloride: m.p. 195-196° (precipitated by ether from alcohol).

β-Form of 1,2,5-Trimethyl-4-piperidinol

Methylation of 5 g of the β-form of 2,5-dimethyl-4-piperidinol (II, m.p. 141-142°) by the above-described procedure yielded 4.3 g of the β-form of 1,2,5-trimethyl-4-piperidinol (VII), m.p. 77-78°: long plates, soluble in water and organic solvents.

Found %: N 9.77

$C_9H_{17}ON$. Calculated %: N 9.78

Picrate: fine, matted needles, m.p. 181-182°. Hydrochloride: hygroscopic crystals, deliquescing in air.

Benzoic Ester of the α-Form of 1,2,5-Trimethyl-4-piperidinol

A mixture of 4.5 g of the hydrochloride of the α-form of 1,2,5-trimethyl-4-piperidinol (m.p. 196°) and 6 g of freshly distilled benzoyl chloride was heated at 150° until evolution of hydrogen chloride ceased (20-30 minutes). The cooled thick mass was dissolved in water, extracted three times with ether, and decomposed with a saturated solution of sodium carbonate. The base, which floated on the surface, was extracted with ether, and the ether extract was dried with potassium carbonate and vacuum-distilled, yielding 5.2 g of the benzoic ester of the α-form of 1,2,5-trimethyl-4-piperidinol (VIII) in the form of an almost colorless oil, b.p. 135-136° (2 mm); n_D^{20} 1.5170; d_4^{20} 1.0315; Found MR 72.22; Calculated MR 71.26.

Found %: N 5.45

$C_{16}H_{21}O_2N$. Calculated %: N 5.67

Picrate: needles, m.p. 199-200° (from methanol).

Found %: N 12.26, 12.19

$C_{22}H_{24}O_9N_4$. Calculated %: N 11.76

Hydrochloride: large needles, formed into clusters, m.p. 201-202° (precipitated by ether from alcohol); readily soluble in water and alcohol.

Benzoic Ester of the β-Form of 1,2,5-Trimethyl-4-piperidinol

Benzoylation of 6 g of the hydrochloride of the β-form of 1,2,5-trimethyl-4-piperidinol (m.p. 182°) by the above-described procedure yielded 8.5 g of the benzoic ester of the β-form of 1,2,5-trimethyl-4-piperidinol (VIII) in the form of an oil, b.p. 128-130° (2 mm); n_D^{20} 1.5190; d_4^{20} 1.0440; Found MR 71.8; Calculated MR 71.26

Found %: N 5.9

$C_{16}H_{21}O_2N$. Calculated %: N 5.67

Picrate: fine needles, m.p. 217-218° (from methanol).

Found %: N 12.03, 11.95

$C_{22}H_{24}O_9N_4$. Calculated %: N 11.76

Hydrochloride: thick noncrystallizing mass.

Benzoic Ester of the γ-Form of 1,2,5-Trimethyl-4-piperidinol

A mixture of 4.55 g of the benzoic ester of the γ-form of 2,5-dimethyl-4-piperidinol (IV), 1.88 g of 32% formaldehyde, and 1 g of 90% formic acid was heated in a boiling water bath until evolution of carbon dioxide ceased (40 minutes). The product was washed with sodium carbonate and extracted with ether; the ether extract was dried with sodium sulfate. Vacuum distillation yielded 4.1 g of the benzoic ester of the γ-form of 1,2,5-trimethyl-4-piperidinol (VIII) in the form of a colorless oil, b.p. 136-137° (2.5 mm); n_D^{20} 1.5195; d_4^{20} 1.0399; Found MR 72.15; Calculated MR 71.26.

$C_{15}H_{21}O_2N$. Found %: N 6.77; Calculated %: N 5.67

Picrate: fine square plates, m.p. 181-182° (from methanol). Hydrochloride (precipitated with ether from alcohol): crystals, m.p. 178-179.5°, readily soluble in water and alcohol.

γ-Form of 1,2,5-Trimethyl-4-piperidinol

A mixture of 3.15 g of the benzoic ester of 1,2,5-trimethyl-4-piperidinol (VIII) and 40 ml of 25% hydrochloric acid was heated in a boiling water bath for two hours. Benzoic acid was filtered off, and the mother liquor was evaporated and treated with caustic soda. The base was extracted with ether, and the ether extract was dried with potassium carbonate. Vacuum distillation yielded 1.1 g of the γ-form of 1,2,5-trimethyl-4-piperidinol (VII) in the form of a liquid, b.p. 88° (6 mm).

$C_8H_{17}ON$. Found %: N 9.70, 9.71; Calculated %: N 9.78

Picrate: small oblong plates, m.p. 167-168° (from methanol).

$C_{14}H_{20}O_8N_4$. Found %: N 14.94, 14.93; Calculated %: N 15.05

Hydrochloride: hygroscopic mass that did not readily crystallize.

Picrates of 2,5-Dimethyl-4-piperidone (I)*

a) Equimolecular proportions of 2,5-dimethyl-4-piperidinol (0.5 g) and picric acid (0.9 g) were dissolved in 5 ml of methanol. After some evaporation, followed by cooling, 1.04 g of a picrate was precipitated in the form of large yellow rods, m.p. 168-169°. The evaporated mother liquid, on standing, yielded a further 0.24 g of a picrate having the same melting point. Altogether, therefore, 1.3 g (93%) was obtained. The picrate was very soluble in methanol.

$C_{19}H_{16}O_8N_4$. Found %: C 43.33, 43.49; H 4.70, 4.63; N 15.85, 15.73; Calculated %: C 43.84; H 4.53; N 15.73

When this picrate (20 g) was decomposed with aqueous potassium carbonate, the product was the piperidone (I), b.p. 16-17°; n_D^{20} 1.4656; d_4^{20} 0.9745; Found MR 36.07; Calculated MR 35.96. The above-described picrate of m.p. 168-169° (1.4 g) was dissolved by heating it with 5 ml of methanol, and one molecular proportion (0.5 g) of 2,5-dimethyl-4-piperidone was added. The solution was boiled in a water bath for ten minutes. From the cooled solution 1.4 g (74%) of yellow needles of a picrate, m.p. 137-138°, separated.

b) Two molecular proportions (1.0 g) of 2,5-dimethyl-4-piperidone were added to a cold solution of one molecular proportion (0.9 g) of picric acid in 5 ml of methanol, and 1.6 g (84%) of a picrate of m.p. 137-138° was isolated (yellow needles). This picrate is difficultly soluble in methanol.

$C_{30}H_{28}O_{16}N_8$. Found %: C 47.82, 47.88; H 5.50, 5.54; N 15.11, 15.06; Calculated %: C 49.68; H 6.05; N 14.49

The picrate of m.p. 137-138° (20 g) was decomposed with potassium carbonate, yielding 2,5-dimethyl-4-piperidone, b.p. 75-76° (n_D^{20} 1.4652; d_4^{20} 0.9767; Found MR 35.96; Calculated MR 35.96); it crystallized on cooling in beautiful nodules, m.p. 16-17°. The picrate of m.p. 137-138° (0.95 g) was dissolved in 7 ml of methanol, and one molecular proportion (0.45 g) of picric acid was added. The solution was boiled for about ten minutes. On standing, the solution yielded 0.84 g of the above-described picrate, m.p. 168-169° (rods).

* The picrates of 2,5-dimethyl-4-piperidone were investigated by G. S. Litvinenko.

The Dimethyl Ketal (IX)

2,5-Dimethyl-4-piperidone (44 g) was added carefully to a hot saturated solution of an equimolecular proportion (80 g) of picric acid in methanol. As the piperidone was added the methanol boiled gently. The picrate that precipitated from the cool solution was subjected to repeated fractional crystallization from methanol, and as a result 48 g of the above-described picrate of m.p. 168-169° was obtained together with 34 g of the picrate of the dimethyl ketal (IX), m.p. 122-123°.

	Found %:	C 43.70, 43.87; H 5.63, 5.64; N 14.87, 14.9
$C_{18}H_{22}O_9N_4$	Calculated %:	C 44.76; H 5.51; N 13.92

The picrate of m.p. 122-123° (25 g) was ground to a powder and mixed with 100 ml of 25% potassium carbonate. The mixture was shaken for two hours, and potassium picrate was filtered off and washed twice with water. The filtrate was united with the washings and saturated with potassium carbonate, and the free base was carefully extracted with ether. The ether extract was dried with potassium carbonate. Vacuum distillation yielded 9.6 g (90%) of the dimethyl ketal (IX) in the form of a colorless oil, b.p. 81-82° (6 mm); n_D^{20} 1.4595; d_4^{20} 0.9869; Found MR 47.98 Calculated MR 48.44.

	Found %:	C 61.64, 61.67; H 10.76, 10.79; N 7.73, 7.85
$C_9H_{19}O_2N$.	Calculated %:	C 62.43; H 10.98; N 8.09

Hydrolysis of the Dimethyl Ketal (IX)

The ketal (IX) of b.p. 81-82° (6 mm) (7.01 g) was heated in a water bath with 50 ml of dilute hydrochloric acid (1:1) for five hours, and 10 ml of a liquid containing methanol was then distilled off. The residue was saturated with solid caustic potash, and the piperidone that floated to the surface was extracted with ether. The ether extract was dried with potassium carbonate. Vacuum distillation yielded 4.72 g of 2,5-dimethyl-4-piperidone, b.p. 71-72° (5 mm); n_D^{20} 1.4658; d_4^{20} 0.9743, which gave a picrate, m.p. 168-169°, undepressed by an authentic sample. The 10-ml aqueous distillate, after salting out with potassium carbonate and distillation, yielded 0.68 g of methanol, b.p. 63-65°, identified by oxidation to formaldehyde in presence of hot copper gauze.

Oxidation of the α-, β-, and γ-Forms of 2,5-Dimethyl-4-piperidinol (M.p. 98°, 142°, and 87°)

The α-form of 2,5-dimethyl-4-piperidinol (m.p. 97-98°, 1.8 g) was dissolved in Beckmann's mixture (34 ml) and heated at 60° for 30 minutes. The mixture was set aside for 20 hours at room temperature, and then treated with a 50% solution of caustic potash. The base was extracted with ether, and the ether layer was dried with potassium carbonate. Vacuum distillation yielded 0.95 g of 2,5-dimethyl-4-piperidone, b.p. 70-71° (5 mm); n_D^{20} 1.4670; d_4^{20} 0.9741; Found MR 36.17; Calculated MR 35.94. Picrate: large yellow rods, m.p. 168-169°, undepressed by the corresponding picrate obtained from 2,5-dimethyl-4-piperidone.

The β- and γ-forms of 2,5-dimethyl-4-piperidinol (m.p. 142° and 87° respectively) were oxidized by the above-described procedure. The piperidones so obtained gave the same picrate of m.p. 168-169°.

SUMMARY

1. Methods have been developed for the preparation of three stereoisomers of 2,5-dimethyl-4-piperidinol (II), and numerous derivatives of these have been described.

2. By the methylation of the isomeric piperidinols (II), three stereoisomeric 1,2,5-trimethyl-4-piperidinols (VII) have been prepared, and a number of their derivatives have been described. All of the stereoisomeric benzoic esters that we have prepared (IV and VIII) have been tested for their activity as local anesthetics.

Received October 20, 1952.

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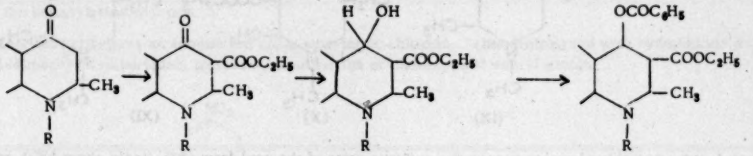
* See Consultants Bureau Translation, page 891.

HETEROCYCLIC COMPOUNDS

COMMUNICATION XXX. CONDENSATION OF 4-PIPERIDONES WITH FORMIC, OXALIC, CARBONIC, AND CHLOROFORMIC ESTERS. SYNTHESIS OF COCAINE ANALOGS*

I. N. Nazarov, D. V. Sokolov, and G. S. Litvinenko

The various 4-piperidones that have now become readily available [1] are very important starting materials for the synthesis of new medicinals that can act as substitutes for morphine and cocaine. From 4-piperidones, Nazarov and coworkers have synthesized, in particular, the new sedative promedol, the activity of which is several times as great as that of morphine, and which has a number of other valuable advantages (low toxicity, not habit-forming, no secondary action). The local anesthetic cocaine is another important natural alkaloid, and although there are a large number of synthetic cocaine substitutes (novocaine, dicaine, etc.), the problem of finding new effective anesthetics is still of great importance. With this problem in view we decided to study the ester condensations of 4-piperidones (I) in order to obtain oxopiperidinecarboxylic esters (II) and convert them into the corresponding cocaine analogs (IV):



(I) (II) (III) (IV)

The ester condensations of 4-piperidones have received little study, there being only isolated communications on this subject in the literature [2]. A number of oxopiperidinecarboxylic esters of the type (II) have been prepared by cyclization of esters of 3,3'-iminodipropionic acids [3].

When 1,2,5-trimethyl-4-piperidone (V) was heated with diethyl carbonate in presence of sodium in absolute xylene at 95-100°, the following substances were isolated: 1,2,5-trimethyl-4-piperidinol (VI), (yield about 20%), ethyl 1,2,5-trimethyl-4-piperidyl carbonate (VII), (yield about 40%), and bis(1,2,5-trimethyl-4-piperidyl) carbonate (VIII), (yield about 15%).

Hence instead of normal ester condensation the piperidone (V) merely underwent reduction to a mixture of the stereoisomers of the piperidinol (VI), which then reacted with diethyl carbonate to give the carbonic esters (VII) and (VIII). The structures of these esters were proved by hydrolysis with 22% hydrochloric acid to the piperidinol (VI), identified by conversion to the benzoic ester (IX), which was formed also as a result of transesterification when the carbonic ester (VII) was heated with benzoyl chloride.

When the carbonic ester (VII) was hydrolyzed, not only the piperidinol (VI) was obtained, but also a small amount of the piperidone (V), which could be formed by the hydrolysis and decarboxylation of the keto ester (X), present as impurity. Reaction of the piperidone (V) with diethyl carbonate in presence of sodium ethoxide resulted in the formation of only the piperidinol (VI), it being found difficult to isolate any other products in a pure state. The same result was obtained when the piperidone (V) was heated with ethyl formate in presence of sodium methoxide:

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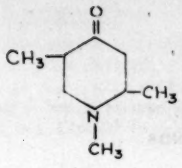
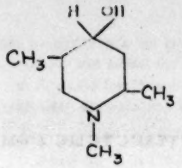
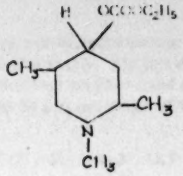


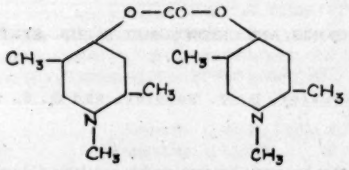
(V)



(VI)



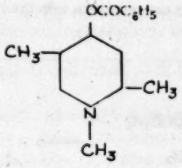
(VII)



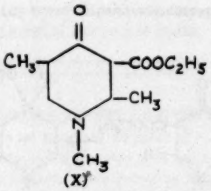
(VIII)

again only reduction to the piperidinol (VI) occurred (yield about 35%).

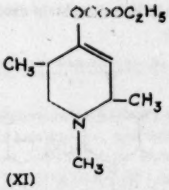
When the piperidone (V) was heated with sodium in absolute xylene, a white precipitate of the sodium derivative readily formed. The sodium derivative gave the original piperidone when hydrolyzed with water, and when



(IX)

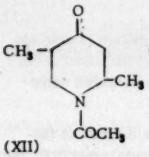


(X)

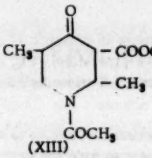


(XI)

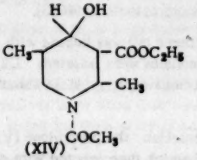
treated with ethyl chloroformate it gave the carbonic ester of the enol form (XI), (yield about 25%), which was reconverted to the piperidone (V) when hydrolyzed with hydrochloric acid. Attempts to effect the condensation of the piperidone (V) with diethyl oxalate (in presence of sodium and of sodium ethoxide) were not successful owing to resinification.



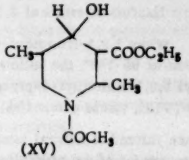
(XII)



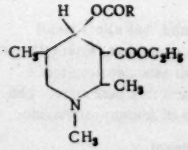
(XIII)
m.p. 65-66°



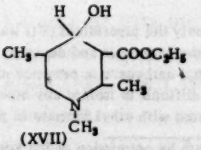
(XIV)
α) m.p. 101-102°
β) not isolated



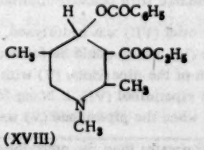
(XV)
α) m.p. 115-116°
β) m.p. 158-159°



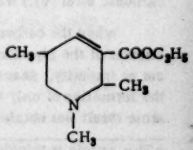
(XVI) mixture of isomers



(XVII)
α) liquid; β) m.p. 87-88°



(XVIII)
α) liquid; β) m.p. 59-60°



(XIX)

Completely different results were obtained when carbonic, formic, and oxalic esters were condensed with 1-acetyl-2,5-dimethyl-4-piperidone (XII). As in the case of alicyclic ketones, all these condensations went normally (60-70% yields), a consequence of the neutralization of the basic properties of the amine nitrogen by acetylation.

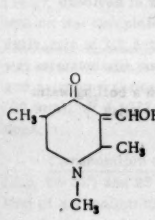
Condensation of 1-acetyl-2,5-dimethyl-4-piperidone (XII) with diethyl carbonate in presence of sodium or sodium ethoxide yielded the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (XIII), which was hydrogenated in presence of a nickel catalyst to a mixture of stereoisomers of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid (XIV). This last compound has four asymmetric carbon atoms, and may exist in the form of eight racemates. From the mixture of stereoisomers of the ester (XIV) we succeeded in isolating only one individual isomer, the α-isomer, m.p. 101-102°.

When the mixture of stereoisomeric acetyl esters (XIV) was heated with hydrochloric acid or with an alcoholic solution of hydrogen chloride, the acetyl group was split off, and a mixture of stereoisomers of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (XV) was formed, from which two individual isomers, m.p. 115-116° and 158-159°, were isolated. The low-melting α-isomer, m.p. 115-116°, was obtained also by deacetylation of the α-isomer of the acetyl nipecotic ester (XIV), m.p. 101-102°. Methylation of the individual α- and β-isomers of the piperidinol (XV) with formaldehyde and formic acid yielded the α- and β-isomers of the ethyl ester of 4-hydroxy-1,2,5-trimethylnipecotic acid (XVII), which were converted by means of benzoyl chloride into the individual α- and β-isomers of the benzoic ester (XVIII).

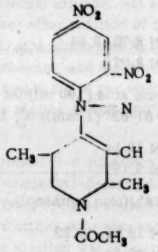
The crystalline β-isomer of (XVII) (m.p. 87-88°) benzoylated very smoothly, whereas the liquid α-isomer of (XVII) was partially dehydrated to the unsaturated ester (XIX). The difference in the behavior of the α- and β-isomers of the piperidinol (XVII) in the benzoylation reaction is probably to be explained by a difference in the spatial disposition of their hydroxyl groups.

When the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid (XIV) was benzoylated with benzoyl chloride and then deacetylated by means of hydrogen chloride, the products, obtained as mixtures of isomers, were the ethyl ester of 4-benzoyloxy-2,5-dimethylnipecotic acid (XVI, R = C_6H_5) and the corresponding acetoxy compound (XVI, R = CH_3). The latter compound was formed as a result of transfer of acetyl from nitrogen to oxygen in the course of the benzoylation reaction.

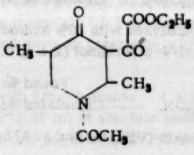
The keto ester (XIII) gave an intense red color with ferric chloride. When hydrolyzed with hydrochloric acid, it yielded 2,5-dimethyl-4-piperidone, formed by elimination of carboxyl and acetyl groups.



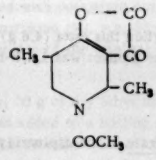
(XX)



(XXI)



(XXII)



(XXIII)

When 1-acetyl-2,5-dimethyl-4-piperidone (XII) was condensed with ethyl formate in presence of sodium ethoxide in dry benzene solution, a 68% yield of the crystalline formyl derivative (XX) (shown in its hydroxymethylene enol form) was obtained; this gave an intense red color with ferric chloride, and gave the pyrazole derivative (XXI) with 2,4-dinitrophenylhydrazine. When 1-acetyl-2,5-dimethyl-4-piperidone (XII) reacted under the same conditions with diethyl oxalate, a 70% yield of the crystalline lactone (XXIII) was formed as a result of the cyclization of the oxalic ester (XXII). When the lactone (XXIII) was heated with alcohol, it was reconverted into the oxalic ester (XXII), which is an oil, but it was not found possible to isolate the latter in the pure state, for when this compound was heated, elimination of alcohol readily occurred with formation of the lactone (XXIII).

Hence, the piperidone oxalyl derivative (XXII) differs greatly in its behavior from the oxalyl derivatives of alicyclic ketones, which are considerably more stable.

EXPERIMENTAL

Sodium ethoxide was prepared by dissolving sodium in twenty times its weight of absolute alcohol. The excess of alcohol was distilled off in a bath of Wood's metal, at first at ordinary pressure, and then under somewhat reduced pressure. When a crust of sodium ethoxide began to form at the walls of the flask (which generally occurred when about two-thirds of the alcohol had been distilled off), the full vacuum of the water pump was applied. When the whole of the alcohol had been removed, the sodium ethoxide was held in a vacuum of 10-15 mm at 150-155° for a further 30 minutes, and then cooled down. The solidified alcohol-free foam of sodium ethoxide was broken up with a glass rod and then converted into a powder by energetic shaking of the closed flask. 2,5-Dimethyl-4-piperidone was prepared from 2-methyl-5-hexen-3-yn-2-ol as previously described [1]; b.p. 70-71° (5 mm); n_D^{20} 1.4670. 1-Acetyl-2,5-dimethyl-4-piperidone was prepared by the acetylation of 2,5-dimethyl-4-piperidone as described in the preceding communication [4]; b.p. 110-112° (1 mm); n_D^{20} 1.4913. 1,2,5-Trimethyl-4-piperidone was prepared from 2-methyl-5-hexen-3-yn-2-ol as described previously [1]; b.p. 71-72° (10 mm); n_D^{20} 1.4595. The nickel catalyst was prepared as follows [5]: Powdered nickel-aluminum alloy (10 g) was added in small portions over a period of 30 minutes at 50° to a vigorously stirred solution of 12.8 g of caustic soda in 50 ml of water. The mixture was maintained at this temperature for a further 50 minutes, and the alkali was then washed away with distilled water until the reaction was neutral to litmus. The catalyst was washed several times with 96% alcohol, and then with absolute alcohol.

Condensation of 1,2,5-Trimethyl-4-piperidone with Diethyl Carbonate. a) A flask containing 200 ml of absolute xylene and 9 g of sodium was heated in a water bath to melt the sodium, and the contents were then stirred while a mixture of 42 g of 1,2,5-trimethyl-4-piperidone (V) and 71 g of dry diethyl carbonate (b.p. 124-125°) was added over a period of 20 minutes. During the addition heating was discontinued, for a temperature of 96-98° was maintained by the heat of reaction. Dissolution of sodium was complete 15 minutes after the whole of the piperidone had been added, and the reaction mixture was then stirred for a further period of ten minutes at 94-96°. After removal of solvent the product was hydrolyzed with ice water (100 ml), and saturated first with carbon dioxide, and then with potassium carbonate. The base, which floated to the surface, was extracted with ether, and the ether extract was dried with sodium sulfate. Repeated vacuum fractionation yielded 8 g of 1,2,5-trimethyl-4-piperidinol (VI), b.p. 61-63° (1 mm); n_D^{20} 1.4749; d_4^{20} 0.9840, which was converted, as described in the preceding communication [4], into the benzoic ester (IX), b.p. 136-138° (1 mm); n_D^{20} 1.5170; d_4^{20} 1.031. From the isomeric mixture of benzoic esters obtained, the picrate of the β-form of the benzoic ester of 1,2,5-trimethyl-4-piperidinol, m.p. 216-218°, was isolated, and this gave no depression with an authentic sample. In this experiment, in addition to the piperidinol (VI), 6 g of bis(1,2,5-trimethyl-4-piperidyl)carbonate (VIII) was isolated as a thick yellowish oil, b.p. 129-131° (1 mm); n_D^{20} 1.4836; d_4^{20} 1.018; Found MR 87.65; Calculated MR 87.51.

	Found %:	N 8.72, 8.84
$C_{17}H_{32}O_3N_2$.	Calculated %:	N 8.97

When this ester (4.6 g) was hydrolyzed with 22% hydrochloric acid (100 ml) for 15 hours in a boiling water bath, the product was 1,2,5-trimethyl-4-piperidinol (2.1 g) b.p. 61-62° (1 mm); n_D^{20} 1.4756; d_4^{20} 0.9547

	Found %:	N 10.14
$C_8H_{17}ON$.	Calculated %:	N 9.79

The picrate of the dipiperidyl carbonate (VIII) melted at 215-216° (from methanol).

	Found %:	N 12.64, 12.82
$C_{19}H_{30}O_{10}N_6$.	Calculated %:	N 19.94

In this experiment also 10 g of intermediate fractions and 9 g of resin were obtained.

b) 1,2,5-Trimethyl-4-piperidone (17.6 g) was added to 2.3 g of sodium melted under 80 ml of absolute xylene. The mixture was heated for 30 minutes at 100° (until all of the sodium had dissolved), and diethyl carbonate (24 g) was then added and heating was discontinued. After 30 minutes the mixture was cooled and acidified with hydrochloric acid (1:1). The aqueous layer was saturated with potassium carbonate, and the base was extracted with ether. The ether layer was dried with sodium sulfate, and the ether was driven off, leaving 22 g of a dark-red oil. The whole reaction was repeated three times, and the united crude product (86 g) was repeatedly fractionated under reduced pressure, yielding 3 g of 1,2,5-trimethyl-4-piperidinol (VI) b.p. 62-63° (1 mm); n_D^{20} 1.4751; d_4^{20} 0.9562; 10 g of the above-described bis(1,2,5-trimethyl-4-piperidyl) carbonate (VIII), b.p. 129-131° (1 mm); n_D^{20} 1.4840; d_4^{20} 1.019; which gave 1,2,5-trimethyl-4-piperidinol when hydrolyzed with hydrochloric acid; and 33 g of

ethyl 1,2,5-trimethyl-4-piperidyl carbonate (VII) as a colorless mobile liquid, b.p. 82-84° (1 mm); n_D^{20} 1.4547; d_4^{20} 1.1005; found MR 57.99; calculated MR 58.02.

Found %: N 6.88; 6.94

$C_{11}H_{21}O_2N$. Calculated %: N 6.51

When this ester was heated with benzoyl chloride (two hours at 165-170°), transesterification occurred with formation of the benzoic ester of 1,2,5-trimethyl-4-piperidinol (IX), b.p. 137-139° (1 mm); n_D^{20} 1.5145; d_4^{20} 1.041, identified by isolation of the picrate of the β-form, m.p. 216-216°, and by a mixture melting-point test with an authentic sample.

Hydrolysis of the ester VII with 22% hydrochloric acid at the boil yielded 1,2,5-trimethyl-4-piperidinol, b.p. 91-93° (5 mm); n_D^{20} 1.4748, and a very small amount of 1,2,5-trimethyl-4-piperidinol (V), identified by preparation of the picrate, m.p. 168-169°, and by a mixture melting-point test with an authentic sample.

c) Absolute xylene (100 ml) was added to dry sodium ethoxide powder prepared from 9.2 g of sodium, the temperature of the mixture was raised to 90°, and 1,2,5-trimethyl-4-piperidone (28.6 g) was added. The mixture was stirred for ten minutes, and dry diethyl carbonate (47 g) was added. After 15 minutes, xylene was removed from the yellowish reaction mixture under reduced pressure; the residue was decomposed with ice (80 g), and then saturated first with carbon dioxide and then with potassium carbonate. The red oil that floated on the surface was dried with sodium sulfate and vacuum-fractionated three times, yielding 6.3 of 1,2,5-trimethyl-4-piperidinol, b.p. 59-60° (0.8 mm); n_D^{20} 1.4750; d_4^{20} 0.9566.

Found %: N 9.92; 9.76

$C_8H_{17}ON$. Calculated %: N 9.79

In this experiment, apart from the piperidinol VI, 6 g of higher fractions and 9.4 g of resin were obtained.

d) The condensation with sodium ethoxide was carried out also at room temperature (standing for three days), and 14 g of 1,2,5-trimethyl-4-piperidone, 24 g of diethyl carbonate, and 27 g of dry sodium ethoxide (9.2 g of sodium) yielded 5.2 g of 1,2,5-trimethyl-4-piperidinol (VI), b.p. 99-101° (9 mm); n_D^{20} 1.4748, and 4.5 g of resin. The piperidinol VI was identified by conversion into its benzoic ester (IX) and by isolation of the picrate of the β-form (m.p. 216-218°, undepressed by authentic sample).

Preparation of the Sodium Derivative of 1,2,5-Trimethyl-4-piperidone, and Its Hydrolysis. Sodium (2.3 g) was melted under 50 ml of absolute toluene, the mixture was vigorously stirred, and 1,2,5-trimethyl-4-piperidone (14 g), dissolved in 20 ml of absolute toluene, was added at 97-100° over a period of one hour. Dissolution of the sodium was complete ten minutes after addition of the whole of the piperidone. The white precipitate of the sodium derivative of 1,2,5-trimethyl-4-piperidone that had formed was hydrolyzed with water (30 ml). The aqueous layer was saturated with potassium carbonate, and the product was extracted with toluene, dried with potassium carbonate, and vacuum-fractionated, yielding 9.6 g of the starting material, 1,2,5-trimethyl-4-piperidone (V), b.p. 88-89° (20 mm); n_D^{20} 1.4587; its picrate melted at 168-169°, and gave no depression with the picrate of the original piperidone.

Condensation of 1,2,5-Trimethyl-4-piperidone with Ethyl Formate. A solution of 32 g of dry ethyl formate (b.p. 54-55°) and 28 g of 1,2,5-trimethyl-4-piperidone in 30 ml of absolute benzene was added to a boiling suspension of dry sodium methoxide (from 9.2 g of sodium) in 100 ml of absolute benzene. The mixture was boiled for two hours, and the solvent was distilled off under reduced pressure. The brown residue was dissolved in 75 ml of 15% hydrochloric acid, and the solution was saturated with potassium carbonate. The product was extracted with ether, the ether extract was dried with sodium sulfate, and the ether was driven off. Vacuum fractionation yielded 9 g of 1,2,5-trimethyl-4-piperidinol (VI), b.p. 49-51° (0.5 mm); n_D^{20} 1.4749; d_4^{20} 0.9540; found MR 40.29; calculated MR 40.42.

Found %: N 10.19; 10.04

$C_8H_{17}ON$. Calculated %: N 9.79

The 1,2,5-trimethyl-4-piperidinol (VI) obtained was identified by its conversion into the benzoic ester (IX), b.p. 120-121° (0.5 mm); n_D^{20} 1.5180; d_4^{20} 1.031, and by the isolation from this mixture of stereoisomeric benzoic esters of the picrate of the β-form, m.p. 216-218°, undepressed by an authentic sample. In this experiment, apart from the piperidinol VI, 8.5 g of intermediate fractions and 4.5 g of resin were obtained. When the condensation was carried out in the cold, the piperidinol VI was not formed; the reaction product was a red oil, which did not crystallize and could not be distilled without decomposition at 1 mm. The oil gave an intense red color with ferric chloride.

Condensation of 1,2,5-Trimethyl-4-piperidinol with Ethyl Chloroformate. A solution of 11 g of freshly distilled ethyl chloroformate in 10 ml of dry toluene was added dropwise to a vigorously stirred, cooled (10-12°) suspension of the sodium derivative of 1,2,5-trimethyl-4-piperidone, prepared as described above from 14 g of the piperidone and 2,3 g of sodium. After 30 minutes, the sodium chloride that had formed was washed out with water, and the product was extracted with toluene. The extract was dried with sodium sulfate, the toluene was distilled off, and the residue was vacuum-fractionated three times, yielding 6.3 g of ethyl 1,2,5,6-tetrahydro-1,2,5-trimethyl-4-pyridyl carbonate (XI) as a colorless mobile liquid, b.p. 73-76° (1 mm); n_D^{20} 1.4640; d_4^{20} 1.019; found MR 57.67; calculated MR 57.55.

	Found %:	N 6.85; 6.78
$C_{11}H_{19}O_2N$.	Calculated %:	N 6.57

There were also obtained 1 g of the original 1,2,5-trimethyl-4-piperidone (identified by the picrate), 5 g of intermediate fractions, and 2 g of tar. The picrate of the ester XI melted at 143-144° (from methanol).

	Found %:	N 12.90; 12.84
$C_{17}H_{22}O_{10}N_4$.	Calculated %:	N 12.67

The ester XI (5.3 g) and 100 ml of 22% hydrochloric acid were heated in a boiling water bath for ten hours. The usual treatment yielded 1.6 g of 1,2,5-trimethyl-4-piperidone (V), b.p. 64-65° (5 mm); n_D^{20} 1.4590, which gave a picrate of m.p. 168.5-169°, undepressed by an authentic sample.

Condensation of 1-Acetyl-2,5-dimethyl-4-piperidone with Diethyl Carbonate. a) In a flask fitted with mechanical stirrer and reflux condenser protected with a calcium chloride tube, a mixture of 25.4 g (0.15 mole) of 1-acetyl-2,5-dimethyl-4-piperidone (XII), 35.4 g (0.3 mole) of diethyl carbonate (b.p. 125-126°; dried over sodium), and 4.5 g of sodium was heated until the sodium melted (100°). Exothermic reaction accompanied by frothing set in. After 30 minutes the reaction mixture was cooled, hydrolyzed with water (about 30 ml), and acidified with hydrochloric acid. The product was extracted with benzene, and the extract was dried with sodium sulfate. After removal of solvent, two vacuum fractionations yielded 12 g (33%) of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (XIII) as a thick colorless oil, b.p. 136-138° (1.5 mm); n_D^{20} 1.4975; d_4^{20} 1.1245; found MR 62.75; calculated MR for the keto form 61.04, and for the enol form 62.08.

	Found %:	N 5.67; 5.98
$C_{13}H_{19}O_4N$.	Calculated %:	N 5.81

The condensation product gave an intense red color with an alcoholic solution of ferric chloride. During the condensation much resinification occurred: 13.9 g of resin remained after the fractionations. When a lower excess (20%) of diethyl carbonate was used, the yield was reduced to 16%.

b) A mixture of 25.4 g of 1-acetyl-2,5-dimethyl-4-piperidone, 35.4 g of diethyl carbonate, and sodium ethoxide powder obtained from 6.9 g of sodium was stirred at 90° for 40 minutes. The product was hydrolyzed with water (40 ml), acidified with concentrated hydrochloric acid, saturated with common salt, extracted with benzene, dried with sodium sulfate, and vacuum-fractionated, yielding 13.2 g (36.5%) of the above-described ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (XIII), b.p. 141-142° (1.7 mm); n_D^{20} 1.4982; d_4^{20} 1.1243.

	Found %:	N 6.29; 6.23
$C_{13}H_{19}O_4N$.	Calculated %:	N 5.81

A residue of 11.2 g of resin remained in the flask. When the condensation temperature was reduced, the yield was progressively improved: 42% at 80°, and 54% at room temperature (15-20°). When a lower excess (30%) of diethyl carbonate was used, the yield obtained at room temperature was reduced to 46%. The best yield (55%) was obtained when the condensation was carried out as described below.

c) A mixture of 25.4 g of 1-acetyl-2,5-dimethyl-4-piperidone, 35.4 g of dry diethyl carbonate, and sodium ethoxide powder prepared from 4.6 g of sodium was kept in a closed flask at 15-20° for ten days. The product was treated as described above, and yielded 20 g (55%) of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (XIII), b.p. 134-136° (1 mm); n_D^{20} 1.4938. After long standing the product crystallized, and it was recrystallized from petroleum ether in the form of needles, which formed rodlike clusters, m.p. 65-66°.

	Found %:	N 6.07; 5.77
$C_{13}H_{19}O_4N$.	Calculated %:	N 5.81

Hydrolysis of the Ethyl Ester of 1-Acetyl-2,5-dimethyl-4-oxonipecotic Acid. A mixture of 8.1 g of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (b.p. 134-136°/1 mm) and 100 ml of 22% hydrochloric acid was heated in a boiling water bath for 32 hours. The hydrochloric acid was distilled off under reduced pressure,

and the residue was dissolved in water. The aqueous solution was saturated with potassium carbonate, and the base was extracted with ether, dried with potassium carbonate, and vacuum-distilled, yielding 2.5 g of 2,5-dimethyl-4-piperidone, b.p. 72-73° (6 mm); n_D^{20} 1.4670. Its picrate melted at 168-169° and gave no depression with the picrate of authentic 2,5-dimethyl-4-piperidone.

Hydrogenation of the Ethyl Ester of 1-Acetyl-2,5-dimethyl-4-oxonipecotic Acid. Nickel catalyst (about 5 g) was added to a solution of 16 g of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (b.p. 134-136°/1 mm) in 80 ml of absolute alcohol. In the course of 14 hours' shaking, 1.65 liter of hydrogen was absorbed, against 1.66 liter required by theory. The solution gave no color with ferric chloride. After filtration from catalyst and removal of alcohol, the hydrogenation product was vacuum-fractionated, yielding

Fraction I, b.p. 151-156° (1 mm), 2.5 g
Fraction II, b.p. 156-161° (1 mm), 5.7 g
Fraction III, b.p. 161-170° (1 mm), 5.9 g

All three fractions were mixtures of stereoisomers of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid (XIV).

Fraction I, b.p. 151-156° (1 mm); n_D^{20} 1.4402; d_D^{20} 1.105; found MR 63.58; calculated MR 62.55.

Found %: N 6.00; 6.06
$C_{12}H_{21}O_4N$. Calculated %: N 5.76

Fraction II, b.p. 156-161° (1 mm); n_D^{20} 1.4902; d_4^{20} 1.1185; found MR 62.85; calculated MR 62.55.

Found %: N 5.90
$C_{12}H_{21}O_4N$. Calculated %: N 5.76

After standing for a long time, this fraction partially crystallized. The crystals were separated and recrystallized from petroleum ether, yielding 1.6 g of an isomer of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid having m.p. 101-102°.

Found %: N 5.80; 5.92
$C_{12}H_{21}O_4N$. Calculated %: N 5.76

Fraction III, b.p. 161-170° (1 mm); n_D^{20} 1.4892; d_4^{20} 1.125; found MR 62.38; calculated MR 62.55.

Found %: N 5.57; 5.95
$C_{12}H_{21}O_4N$. Calculated %: N 5.76

Ethyl Ester of 4-Hydroxy-2,5-dimethylnipecotic Acid. a) A mixture of isomers of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid obtained as described above by the hydrogenation of 14.6 g of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (XIII) in presence of a nickel catalyst was dissolved in 150 ml of absolute alcohol. The solution was saturated with dry hydrogen chloride and boiled under reflux for 28 hours. The solvent was distilled off, and the residue was vacuum-dried and again dissolved in 150 ml of absolute alcohol, saturated with hydrogen chloride, and boiled under reflux for 10 hours. The alcohol was driven off, and the residue of hydrochloride was dissolved in water (30 ml), washed with benzene, decomposed with potassium carbonate, and extracted with ether. During extraction a precipitate formed of the ether-insoluble high-melting β-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (XV), which was recrystallized from dry benzene, yielding 3.4 g of leaves, m.p. 158-159°.

Found %: N 7.10; 7.28
$C_{10}H_{19}O_3N$. Calculated %: N 6.92

Found: M 200.5; 200.4; (titration with 0.1 N HCl with methyl orange indicator)
Calculated: M 201.3

Picrate: yellow hexagonal plates, m.p. 204-205° (from absolute alcohol):

Found %: C 45.07; 44.93; H 5.18; 5.24; N 12.60; 12.52
$C_{16}H_{22}O_{10}N_4$. Calculated %: C 44.65 H 5.15 N 13.03

Hydrochloride: colorless scales, m.p. 198-199° (reprecipitation from alcohol with ether).

The ether extract obtained after separation of crystals of m.p. 158-159° was dried with sodium sulfate, and the solvent was then distilled off. When the oil that remained was vacuum-distilled, it boiled over a wide range (103-180°/1.5 mm), and it was, therefore, again boiled with an anhydrous alcoholic solution of hydrogen chloride (twice: 36 and

17 hours). To the oil obtained after the usual treatment (3.7 g), three times its amount of dry ether was added. The crystals that came down after a while (2.1 g) were recrystallized from dry benzene, and yielded 1.2 g of the low-melting α-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (XV), which formed clusters of needles, m.p. 115-116°.

Found %: N 7.14; 6.77
$C_{10}H_{19}O_3N$. Calculated %: N 6.92

Found: M 200.3; 200.1
Calculated: M 201.3

The product was generally of good solubility in organic solvents, but did not dissolve readily in petroleum ether. It was difficult to recrystallize owing to its tendency to form supersaturated solutions.

Picrate: nodules, m.p. 142-143° (from a mixture of alcohol and petroleum ether).

Found %: N 12.75; 12.84
$C_{16}H_{22}O_{10}N_4$. Calculated %: N 13.03

Hydrochloride: fine crystals, m.p. 185-186° (reprecipitated from alcohol with ether).

In this experiment there was isolated also 2 g of the original ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid, b.p. 145-163° (1 mm); n_D^{20} 1.4902; d_4^{20} 1.118.

b) A solution of 16.2 g of a mixture of isomers of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid, obtained by hydrogenation of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid in presence of a nickel catalyst, in 400 ml of 10% hydrochloric acid was heated in a water bath for 60 hours. The hydrolysis product, after complete removal of hydrochloric acid under reduced pressure, was dissolved in 150 ml of absolute alcohol, and the solution was boiled in presence of hydrogen chloride for 16 hours in order to esterify the carboxyl group. The alcohol was distilled off, the residue was treated with potassium carbonate, and the base was extracted with ether. The substance that was then precipitated was separated and recrystallized from dry benzene, yielding 3.2 g of the ether-insoluble high-melting β-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (XV), m.p. 158-159°. After removal of ether from the ether extract and crystallization of the residue from dry benzene, 2.3 g of the low-melting α-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (XV) of m.p. 115-116° was obtained.

c) A solution of 1.4 g of the crystalline isomer of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid (m.p. 101-102°) in 100 ml of absolute alcohol was saturated with dry hydrogen chloride and boiled under reflux for 30 hours. The usual treatment yielded 0.6 g of the low-melting α-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (XV), m.p. 115-116°, and 0.8 g of the original substance, m.p. 101-102°, was recovered unchanged.

When the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid (16.5 g) was reduced with 2.5% sodium amalgam (750 g) in 45% aqueous alcohol (150 ml), and the product was heated with hydrogen chloride in absolute alcohol to eliminate the acetyl group, the products were 1.4 g of the high-melting β-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid, m.p. 158-159°, and 5 g of a mixture of isomers, b.p. 103-122°/1.5 mm, from which 0.8 g of the low-melting α-isomer, m.p. 115-116°, was isolated.

Ethyl Esters of 4-Acetoxy- and 4-Benzoyloxy-2,5-dimethylnipecotic Acids. Freshly distilled benzoyl chloride (10 g) was heated with 14.3 g of the mixture of isomers of the ethyl ester of 1-acetyl-4-hydroxy-2,5-dimethylnipecotic acid obtained by hydrogenation of the ethyl ester of 1-acetyl-2,5-dimethyl-4-oxonipecotic acid in presence of a nickel catalyst; the temperature was 170°, and heating was continued until evolution of hydrogen chloride ceased (15 minutes). A current of dry hydrogen chloride was then passed through the reaction mixture for one hour at 160°. The product was dissolved in water, washed with benzene, and treated with potassium carbonate. The base was extracted with benzene, dried with sodium sulfate, and vacuum-fractionated, yielding 1.5 g of the ethyl ester of 4-acetoxy-2,5-dimethylnipecotic acid (XVI, R = CH_3), b.p. 101-102° (1 mm); n_D^{20} 1.4610; d_4^{20} 1.065; found MR 62.82; calculated MR 62.32.

Found %: N 6.18; 6.14
$C_{12}H_{21}O_4N$. Calculated %: N 5.76

The fractionation yielded also 0.9 g of the ethyl ester of 4-benzoyloxy-2,5-dimethylnipecotic acid (XVI, R = C_6H_5), b.p. 160-164° (1 mm); n_D^{20} 1.5123; d_4^{20} 1.1145; found MR 82.16; calculated MR 81.81.

Found %: N 4.97; 4.90.
$C_{17}H_{23}O_4N$. Calculated %: N 4.59

Each of these esters is a mixture of stereoisomers, and they give oily picrates and hydrochlorides.

Ethyl Ester of 4-Hydroxy-1,2,5-trimethylnipecotic Acid (XVII, α-isomer). A mixture of 4.4 g of the low-melting α-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (m.p. 115-116°), 3.4 g of 29% formaldehyde, and 1.4 g of 90% formic acid was heated in a boiling water bath until carbon dioxide ceased to be evolved (40 minutes). The cooled solution was treated with potassium carbonate, and the base was extracted with ether, dried with magnesium sulfate, and vacuum-distilled, yielding 4.3 g of the α-isomer of the ethyl ester of 4-hydroxy-1,2,5-trimethylnipecotic acid (XVII), b.p. 112-113° (1 mm); n_D^{20} 1.4778; d_4^{20} 1.0528; found MR 57.86; calculated MR 57.93.

	Found %:	C 62.02; 61.98; H 9.99; 10.04; N 6.58; 6.52
$C_{11}H_{21}O_3N$.	Calculated %:	C 61.36; H 9.83 N 6.51

Found: M 215.4; 214.5 (titration)
Calculated: M 215

Picrate: yellow rods, m.p. 141-142° (from absolute alcohol).

	Found %:	N 12.83; 12.31
$C_{17}H_{24}O_{10}N_4$.	Calculated %:	N 12.61

Hydrochloride: colorless rosettes, m.p. 151-152° (reprecipitated from alcohol with ether).

Ethyl Esters of 4-Benzoyloxy-1,2,5-trimethylnipecotic Acid (XVIII, α-isomer) and of 1,2,5,6-Tetrahydro-1,2,5-trimethylnicotinic Acid (XIX). A mixture of 3.6 g of the above-described hydrochloride of the ethyl ester of 4-hydroxy-1,2,5-trimethylnipecotic acid (m.p. 151-152°) and 6.1 g of freshly distilled benzoyl chloride was heated at 160° until evolution of hydrogen chloride ceased (30 minutes). The excess of benzoyl chloride was distilled off under reduced pressure, and the residue was dissolved in water, washed with ether, and treated with potassium carbonate. The base was extracted with ether, dried with magnesium sulfate, and vacuum-fractionated, yielding 0.7 g of the ethyl ester of 1,2,5,6-tetrahydro-1,2,5-trimethylnicotinic acid (XIX) as a slightly yellowish, mobile oil, b.p. 109-110° (8 mm); n_D^{20} 1.4765; d_4^{20} 0.9940; found MR 56.02; calculated MR 55.94.

	Found %:	N 7.15; 7.16
$C_{11}H_{19}O_2N$.	Calculated %:	N 7.10

Found: M 201.4; 202.3 (titration)
Calculated: M 197.3

Picrate: noncrystallizing oil. Hydrochloride: colorless clusters, m.p. 137-138° (precipitation from alcohol with ether). The fractionation yielded also 2 g of the ethyl ester of 4-benzoyloxy-1,2,5-trimethylnipecotic acid (XVIII, α-isomer) as a greenish oil, b.p. 167-170° (2 mm); n_D^{20} 1.5105; d_4^{20} 1.0873; found MR 87.97; calculated MR 86.78.

	Found %:	N 4.78; 4.55
$C_{18}H_{25}O_4N$.	Calculated %:	N 4.39

Picrate: yellow plates, m.p. 184-185° (from absolute alcohol).

	Found %:	N 10.34; 9.97
$C_{24}H_{28}O_{11}N_4$.	Calculated %:	N 10.22

Hydrochloride: fine colorless leaves, m.p. 185-186° (precipitation from alcohol with ether).

Ethyl Ester of 4-Hydroxy-1,2,5-trimethylnipecotic Acid (β-isomer). The high-melting β-isomer of the ethyl ester of 4-hydroxy-2,5-dimethylnipecotic acid (m.p. 158-159°; 4.1 g) was methylated with formaldehyde and formic acid as described above. Removal of ether, followed by recrystallization of the residue from gasoline (b.p. 80-90°), yielded 3.8 g (88%) of the β-isomer of the ethyl ester of 4-hydroxy-1,2,5-trimethylnipecotic acid (XVII), m.p. 87-88°.

	Found %:	C 61.72; 61.77; H 9.96; 10.05; N 6.53; 6.49
$C_{11}H_{21}O_3N$.	Calculated %:	C 61.36; H 9.83; N 6.51

Found: M 215.2; 215.1 (titration)
Calculated: M 215

Picrate: yellow needles, m.p. 168-169° (from absolute alcohol).

	Found %:	N 12.46; 12.51
$C_{17}H_{24}O_{10}N_4$.	Calculated %:	N 12.61

Hydrochloride: colorless leaves, m.p. 174-175° (reprecipitation from alcohol with ether).

Ethyl Ester of 4-Benzoyloxy-1,2,5-trimethylnipecotic Acid (β-isomer). A mixture of 3.7 g of the hydrochloride of the β-isomer of the ethyl ester of 4-hydroxy-1,2,5-trimethylnipecotic acid (m.p. 174-175°) and 6.3 g of freshly distilled benzoyl chloride was heated at 160° until the evolution of hydrogen chloride ceased (30 minutes). The excess of benzoyl chloride was distilled off under reduced pressure, and the residue was mixed with water (about 15 ml). The crystals that came down were pressed off at the pump and reprecipitated from alcohol with ether, yielding 2.5 g of the hydrochloride of the ethyl ester of 4-benzoyloxy-1,2,5-trimethylnipecotic acid (β-isomer) in the form of leaves of m.p. 213-214°. The aqueous solution remaining after removal of the crystals of hydrochloride was washed with ether and treated with potassium carbonate. The base was extracted with ether and, after being dried with magnesium sulfate, was vacuum-distilled, yielding 1.9 g of the ethyl ester of 4-benzoyloxy-1,2,5-trimethylnipecotic acid (XVIII, β-isomer), b.p. 167-169° (2 mm); n_D^{20} 1.5103; d_4^{20} 1.089; found MR 87.75; calculated MR 86.76. When the amount of hydrochloride isolated was taken into account, the total yield of this benzoic ester was 90%. On standing, the free base crystallized, and recrystallization from petroleum ether yielded rhombic plates, m.p. 59-60°.

	Found %:	C 67.71; 67.86; H 8.01; 7.99; N 4.27; 4.38
$C_{18}H_{25}O_4N$.	Calculated %:	C 67.68; H 7.89; N 4.39

The hydrochloride of this ester melted at 213-214° (precipitated from alcohol with ether) and gave no depression with the above-described hydrochloride, which was directly isolated from the benzoylation products.

Condensation of 1-Acetyl-2,5-dimethyl-4-piperidone with Ethyl Formate. Ethylformate (b.p. 53-54°) (7.1 g) and a solution of 8.1 g of 1-acetyl-2,5-dimethyl-4-piperidone in 150 ml of absolute benzene were added, with continuous stirring and cooling with ice water, to dry sodium ethoxide prepared from 2.2 g of sodium. The mixture was set aside for 40 hours in a hermetically closed flask, and the precipitate that had formed was then filtered off, washed with benzene, and dissolved in presence of small pieces of ice in concentrated hydrochloric acid (20 ml). The solution was saturated with common salt, and the condensation product was extracted with benzene. The extract was dried with sodium sulfate, and, after removal of the greater part of the solvent, the solid present was recrystallized from benzene, yielding 6.5 g (68%) of crystalline 3-hydroxymethylene-1,2,5-trimethyl-4-piperidone (XX), m.p. 123-124°.

	Found %:	N 7.24; 7.29
$C_{10}H_{17}O_2N$.	Calculated %:	N 7.11

In other condensation experiments, the product was vacuum-distilled, and a thick colorless oil, b.p. 138-139°/1 mm, was obtained, which solidified when cold to crystals of m.p. 123-124°. The condensation product (XX) gave an intense red color with ferric chloride. When treated with an alcoholic solution of 2,4-dinitrophenylhydrazine acidified with hydrochloric acid, the condensation product yielded a pyrazole derivative (XXI), m.p. 201-202°.

	Found %:	N 19.66; 19.75
$C_{16}H_{17}O_5N_5$.	Calculated %:	N 19.50

When the formyl derivative XX was hydrogenated in presence of a nickel catalyst, two molecular proportions of hydrogen were absorbed. When the condensation was performed at 80° (at the boil in benzene), the yield of hydroxymethylene derivative (XX) remained practically unchanged. The order in which the piperidone and ethyl formate were added to the sodium ethoxide also had no effect on the yield.

Condensation of 1-Acetyl-2,5-dimethyl-4-piperidone with Diethyl Oxalate. Diethyl oxalate (b.p. 90-91°/15 mm) (29 g) and a solution of 17 g of 1-acetyl-2,5-dimethyl-4-piperidone in 30 ml of absolute benzene were added, with continuous stirring and cooling with ice water, to a suspension of dry sodium ethoxide (obtained from 4.2 g of sodium) in 100 ml of absolute benzene. The reaction mixture was set aside at room temperature overnight, and was then acidified, under cooling, with hydrochloric acid. The condensation product was extracted with benzene, and the white powder that then formed was filtered off, yielding 3.3 g of the lactone XXIII, m.p. 210° (with frothing). The oil remaining after removal of benzene (this oil gave a red color with ferric chloride) was heated for 15 minutes at 150-160°, after which a further 12.2 g of the lactone XXIII was isolated in the form of a white powder, m.p. 211° (with frothing). The total yield of lactone was 15.5 g (68%).

	Found %:	C 59.24; 59.08; H 5.89; 6.15; N 6.29; 6.24
$C_{11}H_{15}O_4N$.	Calculated %:	C 59.19; H 5.83; N 6.28

The lactone was found to have very low solubility in the usual organic solvents and in water. It was readily soluble in alkalis, and was reprecipitated by acid. It gave a green color with an alcoholic solution of ferric chloride.

When boiled with alcohol it was converted into the original oily substance, which gave a red color with ferric chloride, and was probably 1-acetyl-2,5-dimethyl-4-oxo-3-piperidyl ethyl oxalate (XXII). When this condensation was carried out with an alcoholic solution of sodium ethoxide and with sodium in benzene, analogous results were obtained.

SUMMARY

1. The condensations of 1,2,5-trimethyl-4-piperidone and of 1-acetyl-2,5-dimethyl-4-piperidone with diethyl carbonate, with diethyl oxalate, and with ethyl formate have been investigated.

2. It has been shown that in these condensations, 1,2,5-trimethyl-4-piperidone is reduced by the sodium or sodium ethoxide present to 1,2,5-trimethyl-4-piperidinol, whereas 1-acetyl-2,5-dimethyl-4-piperidone gives the normal condensation products in 60-70% yield.

Received October 20, 1952.

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EXCHANGE OF HYDROGEN ATOMS OF SATURATED CYCLIC HYDROCARBONS WITH SULFURIC ACID

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In a previous communication [1] we have described the results of an investigation of the exchange reactivity of the hydrogen atoms of saturated aliphatic hydrocarbons when treated with heavy (deuterium-rich) sulfuric acid. By means of tracer technique we showed that saturated aliphatic hydrocarbons containing tertiary carbon atoms underwent hydrogen exchange in presence of heavy sulfuric acid. On the other hand, saturated aliphatic hydrocarbons in which there were no tertiary carbon atoms did not undergo hydrogen exchange with sulfuric acid.

In the present paper we describe results of an investigation of the exchange reactivity of hydrogen atoms in saturated cyclic hydrocarbons of various structure when treated with heavy sulfuric acid. The constants of the original hydrocarbons are given in Table 1.

TABLE 1

Expt. No.	Hydrocarbon	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
1	Cyclohexane	80.4-80.5 (760)	1.4263	0.7782
2	Methylcyclohexane	100.3-100.4 (755)	1.4230	0.7696
3	1,1-Dimethylcyclohexane	119.9 (760)	1.4294	0.7810
4	1-Ethyl-4-methylcyclohexane (mixture of cis and trans isomers)	149.3-152.2 (760)	1.4326	0.7851
5	1,4-Dimethylcyclohexane (trans isomer)	119.5 (761)	1.4209	0.7627
6	Cyclopentane	49.0 (760)	1.4065	0.7452
7	Methylcyclopentane	71.8 (760)	1.4098	0.7485
8	Decahydronaphthalene (trans isomer)	72.0-72.5 (18)	1.4692	0.8690
9	Decahydronaphthalene (30% cis + 70% trans)	59.6-62.0 (10)	1.4739	–

Treatment with heavy sulfuric acid (monohydrate, or acid containing traces of SO_3) was carried out at 20-25° in sealed tubes, which were placed in a shaker (160-180 shakes per minute)). After the experiment the hydrocarbons were purified as in the case of the acyclic hydrocarbons [1], and were then subjected to combustion over red-hot copper oxide. The water obtained was suitably purified, and the amount of deuterium in the hydrocarbon under investigation was determined from the density excess of this combustion water. Results for hydrogen exchange in hydrocarbons of the cyclohexane series are given in Table 2, and results for cyclopentane hydrocarbons are given in Table 3.

TABLE 2

Expt. No.	Hydrocarbon	Amount (moles)		Duration of reaction (hr)	Excess density of combustion water (γ)			Exchange (% of value calcd. for exchange of all H)
		of acid	of h.c.		calculated* for 1 H	calculated* for all H	found	
1	Cyclohexane	0.050	0.033	3	–	19350	272	1.4
2	Methylcyclohexane	0.054	0.027	3	5532	21418	20915	98
3	Methylcyclohexane	0.058	0.029	10.5	5525	21290	20650	97
4	Methylcyclohexane	0.053	0.022	26	5748	25080	24890	99
5	1,4-Dimethylcyclohexane (trans)	0.040	0.020	12	–	3228	3214	99
6	1-Ethyl-4-methylcyclohexane (mixture of cis and trans)	0.058	0.019	11	–	24235	20100	83
7	1-Ethyl-4-methylcyclohexane (mixture of cis and trans)	0.055	0.012	25	–	5390	5176	96
8	1,1-Dimethylcyclohexane	0.051	0.016	4	–	5000	89	1.8

* In the calculations, the distribution coefficient is taken to be unity.

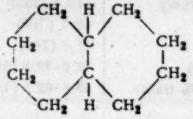
TABLE 3

Expt. No.	Hydrocarbon	Amount (moles)		Duration of reaction (hr)	Excess density of combustion water (γ)			Exchange (% of value calcd. for exchange of all H)
		of acid	of h.c.		calculated for 1 H	calculated for all H	found	
1	Cyclopentane	0.059	0.054	1	–	2980	56	1.9
2	Cyclopentane	0.042	0.022	3	–	4193	98	2.3
3	Cyclopentane	0.045	0.028	50	–	3719	94	2.5
4	Methylcyclopentane	0.021	0.035	1	188	378	202	54
5	Methylcyclopentane	0.060	0.033	1	1116	4014	2118	53
6	Methylcyclopentane	0.046	0.046	2.5	940	2399	1578	66
7	Methylcyclopentane	0.047	0.027	3	984	3362	2526	75
8	Methylcyclopentane	0.041	0.027	4	970	3117	2590	83
9	Methylcyclopentane	0.060	0.033	5	972	3386	2926	90
10	Methylcyclopentane	0.048	0.018	10	1071	4507	4214	94
11	Methylcyclopentane	0.063	0.020	15	1104	5276	5068	96
12	Methylcyclopentane	0.062	0.024	14	1119	4848	4807	99

The results given in Tables 2 and 3 show that the presence in a cycloalkane ring of tertiary carbon atoms greatly influences the reactivity of the whole molecule. Thus, in a cyclohexane ring containing a tertiary carbon atom all the hydrogen atoms become reactive and exchange equilibrium is established at room temperature in several hours (Expt. No. 2, 3, 4, and 5, Table 2), whereas cyclohexane and 1,1-dimethylcyclohexane do not undergo hydrogen exchange (Expt. No. 1 and 8, Table 2).

The cyclopentane hydrocarbons present a similar picture: methylcyclopentane undergoes hydrogen exchange, equilibrium being established in 14-15 hours (Expt. No. 11 and 12, Table 3), whereas cyclopentane shows no appreciable tendency to enter into this reaction (Expt. No. 1, 2, and 3, Table 3).

Investigation of the tendency of trans-decahydronaphthalene (I)



(I)

and a mixture of cis- and trans-decahydronaphthalene to undergo hydrogen exchange led us, however, to unexpected results. On the basis of the results cited above (Tables 2 and 3) it might be expected that the presence in the decahydronaphthalene molecule of two tertiary carbon atoms would make this compound prone to hydrogen exchange in presence of sulfuric acid. It was found, however, that neither of the isomers of decahydronaphthalene underwent hydrogen exchange, even after long contact with sulfuric acid (Table 4). It will be noted that the tertiary carbons of decahydronaphthalene, unlike those in the previously studied compounds, are concerned in bridge formation. The question of exchange reactivity at such carbons is in need of further investigation.

Our investigation has, therefore, shown that the rule determining the tendency for saturated hydrocarbons to undergo hydrogen exchange is general both for aliphatic and cyclic hydrocarbons; as indicated, the only exception is decahydronaphthalene.

TABLE 4

Expt. No.	Hydrocarbon	Amount (moles)		Duration of reaction (hr)	Excess density of combustion water (γ)			Exchange (% of value calcd. for exchange of all H)
		of acid	of h.c.		calculated for 1 H	calculated for all H	found	
1	Decahydronaphthalene (trans)	0.086	0.028	4	1490	4370	80	1.8
2	Decahydronaphthalene (trans)	0.053	0.020	32	1360	3770	91	2.4
3	Decahydronaphthalene (30% cis + 70% trans)	0.049	0.025	11.5	309	683	18	2.6

We have previously suggested that hydrogen exchange with saturated hydrocarbons in presence of sulfuric acid proceeds by a chain mechanism [2]. For the further development of this idea it was of interest to study the exchange reactivity of mixtures of hydrocarbons having tertiary carbons with hydrocarbons that do not contain a tertiary carbon. If in a hydrogen-exchange reaction initiated by a hydrocarbon having a tertiary carbon atom the chain can be propagated via primary and secondary carbon atoms, then the hydrocarbon that does not contain a tertiary carbon will evidently be drawn into the reaction.

In actual fact it was found that whereas the hydrocarbon having a tertiary carbon underwent almost complete hydrogen exchange, the added hydrocarbon that had no tertiary carbon did not enter the exchange reaction. Thus it was found that, when a mixture of n-heptane and methylcyclohexane was treated with heavy sulfuric acid, only the methylcyclohexane underwent hydrogen exchange, the n-heptane being unaffected. These results indicate that the chain is propagated only via tertiary carbon atoms.

EXPERIMENTAL*

1. Cyclohexane and Heavy (Deuterium-rich) Sulfuric Acid. Cyclohexane was prepared by the hydrogenation of repeatedly frozen commercial benzene in an autoclave in presence of a nickel catalyst. The cyclohexane was distilled through a 40-plate column, and was then purified by passage through a column of silica gel. The constants of the cyclohexane were: b.p. 80.4-80.5° (750 mm); d_4^{20} 0.7782; and n_D^{20} 1.4263.

A mixture of 2.73 g (0.033 mole) of cyclohexane and 4.88 g (0.050 mole) of heavy sulfuric acid** (density excess 98980 γ) was agitated in a sealed tube for three hours. After the experiment, the hydrocarbon was washed with 30% caustic potash and with water; it was then dried with potassium carbonate and distilled over sodium. After the experiment the constants of the hydrocarbon were: b.p. 80.2-80.5° (756 mm); n_D^{20} 1.4262; d_4^{20} 0.7788. The water obtained from the combustion of the cyclohexane had a density excess of 272 γ; if all of the twelve hydrogen atoms had undergone exchange with deuterium, the density excess would have been 19,350 γ. The results show that practically no hydrogen exchange occurred between cyclohexane and heavy sulfuric acid.

2. Methylcyclohexane and Heavy Sulfuric Acid. Methylcyclohexane was prepared by the hydrogenation of toluene, which was first purified by conversion into p-toluenesulfonic acid, recovery by hydrolysis, and distillation through a 30-plate column. The hydrogenation was performed in an autoclave in presence of a nickel catalyst. The methylcyclohexane was purified by passage through a silica-gel column, and was then distilled through a 30-plate column. The constants of the methylcyclohexane were: b.p. 100.3-100.4°, (760 mm); d_4^{20} 0.7696; n_D^{20} 1.4230.

A. A mixture of 2.65 g (0.027 mole) of methylcyclohexane and 5.36 g (0.054 mole) of heavy sulfuric acid (96,980 γ) was agitated in a sealed tube for three hours. After the experiment, the hydrocarbon was treated as in Expt. 1, and the final constants of the hydrocarbon were: b.p. 99.5-100° (748 mm); d_4^{20} 0.7914; n_D^{20} 1.4220. The value found for the density excess of the combustion water from the methylcyclohexane was 20,915 γ; value calculated for exchange of all hydrogens with deuterium: 21,418 γ.

B. A mixture of 2.87 g (0.029 mole) of methylcyclohexane and 5.76 g (0.058 mole) of heavy sulfuric acid (96,980 γ) was agitated for 10 hours 30 minutes. After the experiment the constants of the hydrocarbon were: b.p. 99-99.5° at 736 mm; d_4^{20} 0.7914; n_D^{20} 1.4220. The value found for the density excess of the combustion water from the methylcyclohexane was 20,650 γ; value calculated for exchange of all hydrogens: 21,290 γ.

C. A mixture of 2.12 g (0.022 mole) of methylcyclohexane and 5.27 g (0.053 mole) of heavy sulfuric acid (96,980 γ) was agitated for 26 hours. After the experiment the constants of the hydrocarbon were: b.p. 98.5-99.5° at 748 mm; d_4^{20} 0.7971; $n_D^{20.1}$ 1.4220. The value found for the density excess of the combustion water from the methylcyclohexane was 24,890 γ; value calculated for exchange of all hydrogens: 25,060 γ.

The results of Experiments A, B, and C indicate that all the hydrogen atoms enter into the exchange reaction and that exchange equilibrium is established already in three hours.

3. trans-1,4-Dimethylcyclohexane and Heavy Sulfuric Acid. trans-1,4-Dimethylcyclohexane was prepared by the hydrogenation of p-xylene, obtained by the careful purification of the commercial product by repeated freezing. The hydrogenation was performed in presence of platinized charcoal. The 1,4-dimethylcyclohexane was purified by passage through a silica-gel column and distillation through a 75-80-plate column. The fraction taken for investigation had b.p. 119.5° (761 mm); d_4^{20} 0.7627; n_D^{20} 1.4209, which correspond to the constants of trans-1,4-dimethylcyclohexane.

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* A. N. Martynova took part in the experimental work.

** The preparation of the heavy sulfuric acid is described in the previous communication.

A mixture of 2.24 g (0.020 mole) of trans-1,4-dimethylcyclohexane and 8.98 g (0.040 mole) of heavy sulfuric acid (15,990 γ) was agitated in a sealed tube for 12 hours. After the experiment the hydrocarbon was purified in the usual way, and had d_4^{20} 0.7686, $n_D^{20.2}$ 1.4220. The value found for the density excess of the combustion water from the trans-1,4-dimethylcyclohexane was 3214 γ.* The results show that all of the hydrogen atoms of 1,4-dimethylcyclohexane took part in the exchange reaction, but it appears that, under the conditions of the experiment, the hydrocarbon underwent isomerization (evidenced by the change in the constants of the hydrocarbon).

4. 1-Ethyl-4-methylcyclohexane and Heavy Sulfuric Acid. 1-Ethyl-4-methylcyclohexane was prepared as follows: p-toluidine, purified by two recrystallizations from isooctane, was converted by the Sandmeyer reaction into p-bromotoluene, which was then converted into 1-ethyl-4-methylbenzene by the Wurtz reaction; this was then hydrogenated in presence of platinized charcoal at 175°. The hydrogenated product was purified by passage through a silica-gel column and distillation through a 75-80-plate column. The fraction taken for investigation (intermediate between the cis and trans isomers) boiled over the range 149.3-152.2° (760 mm); d_4^{20} 0.7851; n_D^{20} 1.4326.

A. A mixture of 2.36 g (0.019 mole) of 1-ethyl-4-methylcyclohexane and 5.85 g (0.058 mole) of heavy sulfuric acid (94,000 γ) was agitated for 11 hours. After the experiment the hydrocarbon was purified in the usual way, and its constants were $d_4^{20.1}$ 0.8064; $n_D^{20.1}$ 1.4302. The value found for the density excess of the combustion water was 20,100 γ, and the value calculated for exchange of all seventeen hydrogens was 24,232 γ.

B. A mixture of 1.50 g (0.012 mole) of 1-ethyl-4-methylcyclohexane and 5.36 g (0.054 mole) of heavy sulfuric acid (16,000 γ) was agitated for 25 hours. After the experiment the constants of the hydrocarbon were d_4^{20} 0.7884; $n_D^{20.4}$ 1.4312. The value found for the density excess of the combustion water was 5176 γ, and the value calculated for exchange of all seventeen hydrogens was 5390 γ.

From these results it will be seen that exchange equilibrium between 1-ethyl-4-methylcyclohexane and heavy sulfuric acid is established more slowly than for methylcyclohexane and heavy sulfuric acid and that, under these conditions, exchange is apparently accompanied by partial isomerization of the hydrocarbon.

5. 1,1-Dimethylcyclohexane and Heavy Sulfuric Acid. 1,1-Dimethylcyclohexane was prepared by the hydrogenation of dimedon [3]. The hydrocarbon was purified by distillation through a 40-plate column, and its constants were: b.p. 119.9° (760 mm); d_4^{20} 0.7810; n_D^{20} 1.4294. A mixture of 1.74 g (0.016 mole) of 1,1-dimethylcyclohexane and 5.05 g (0.051 mole) of heavy sulfuric acid was agitated for four hours. After the experiment the purified hydrocarbon had the following constants: d_4^{20} 0.7819; $n_D^{20.3}$ 1.4293. The value found for the density excess of the combustion water was 89 γ, and the value calculated for exchange of all 16 hydrogen atoms was 5000 γ. These results indicate that 1,1-dimethylcyclohexane does not undergo hydrogen exchange with heavy sulfuric acid.

6. Cyclopentane and Heavy Sulfuric Acid. Cyclopentane was prepared by the method developed by Kazansky, Terentyeva, and Bulanova [4]. It was distilled through a 40-plate column, and its constants were: b.p. 49.0° (760 mm); d_4^{20} 0.7452; n_D^{20} 1.4065.

A. A mixture of 3.80 g (0.054 mole) of cyclopentane and 5.80 g (0.059 mole) of heavy sulfuric acid (17,000 γ) was agitated for one hour. After the experiment the hydrocarbon was purified in the usual way and had the following constants: b.p. 48.5-49.0° (750 mm); d_4^{20} 0.7456; $n_D^{20.6}$ 1.4062. The value found for the density excess of the combustion water from the cyclopentane was 56 γ, and the value calculated for exchange of all ten hydrogen atoms was 2980 γ.

B. A mixture of 1.56 g (0.022 mole) of cyclopentane and 4.24 g (0.042 mole) of heavy sulfuric acid (15,300 γ) was agitated for three hours. The value found for the density excess of the combustion water was 98 γ, and the value calculated for exchange of all hydrogen atoms was 4193 γ.

C. A mixture of 1.95 g (0.028 mole) of cyclopentane and 4.38 g (0.045 mole) of heavy sulfuric acid was agitated for 50 hours. After the experiment the constants of the hydrocarbon were: 48.5-49° (751 mm); n_D^{20} 1.4062; d_4^{20} 0.7451. The value found for the density excess of the combustion water was 94 γ, and the value calculated for exchange of all hydrogen atoms was 3719 γ.

The results of Experiments A, B, and C indicate that, even when contact with heavy sulfuric acid is prolonged, cyclopentane undergoes practically no hydrogen exchange.

7. Methylcyclopentane and Heavy Sulfuric Acid. Methylcyclopentane was prepared by isomerization of cyclohexene in presence of aluminum oxide into methylcyclopentenes [5], which were then distilled through a 35-plate column and hydrogenated at room temperature in presence of a platinum catalyst. The hydrogenation product was purified by distillation through a 50-plate column. The constants of the methylcyclopentane were: b.p. 71.8° (760 mm); n_D^{20} 1.4098; d_4^{20} 0.7485. Samples of methylcyclopentane were shaken with heavy sulfuric acid of

* The value calculated for exchange of all hydrogens was 3228 γ.

various deuterium contents for various times. After the experiments the hydrocarbon was purified in the usual way and was subjected to combustion over copper oxide. The course of the hydrogen-exchange reaction was characterized by the value of the density excess of the combustion water. The results of the experiments are given in Table 5; they show that exchange equilibrium between methylcyclopentane and heavy sulfuric acid is established in 14-15 hours.

TABLE 5

Expt. No.	Amt. (moles) of substance taken for reaction		Equiv. density excess of acid (γ)	Duration of reaction (hr)	Constants of hydrocarbon		Density excess of combustion water of hydrocarbon (γ)		Exchange (% of value calcd. for exchange of all hydrogen)
	methylcyclopentane	heavy sulfuric acid			n_D^{20}	d_4^{20}	calcd. for all H	found	
1	0.035	0.021	4136	1	–	–	378	202	54
2	0.033	0.060	17000	1	–	–	4014	2118	53
3	0.046	0.046	17000	2.5	–	–	2399	1578	66
4	0.027	0.047	15300	3	1.4100	0.7507	3362	2526	75
5	0.027	0.041	15500	4	–	–	3117	2590	83
6	0.033	0.060	15000	5	–	–	3386	2926	90
7	0.018	0.048	15300	10	1.4097	0.7539	4507	4214	94
8	0.020	0.063	15300	15	1.4095	0.7536	5289	5068	96
9	0.024	0.062	16000	14	–	–	4848	4807	99

8. Decahydronaphthalene and Heavy Sulfuric Acid. A. trans-Decahydronaphthalene, having the constants b.p. 72.0-72.5° at 18 mm; d_4^{20} 0.8690; n_D^{20} 1.4892, was prepared by isomerization of commercial decahydronaphthalene in presence of aluminum chloride [6]. The isomerizate was distilled through a 35-plate column. A mixture of 3.80 g (0.028 mole) of trans-decahydronaphthalene and 8.44 g (0.086 mole) of heavy sulfuric acid (17,000 γ) was agitated for four hours. After the experiment the constants of the hydrocarbon were: b.p. 184-184.5° (737 mm); n_D^{20} 1.4689. The value found for the density excess of the combustion water was 80 γ, and the value calculated for exchange of all hydrogen atoms was 4371 γ.

B. A mixture of 2.85 g (0.020 mole) of trans-decahydronaphthalene and 5.23 g (0.053 mole) of heavy sulfuric acid (17,000 γ) was agitated for 32 hours. After the experiment the constants of the hydrocarbon were: b.p. 55.7-56.2° (8 mm); d_4^{20} 0.8696; $n_D^{20.3}$ 1.4689. The value found for the density excess of the combustion water was 91 γ, and the value calculated for exchange of all hydrogen atoms was 3772 γ.

It may be concluded on the basis of the results of Experiments A and B that trans-decahydronaphthalene does not undergo hydrogen exchange with heavy sulfuric acid to any appreciable extent.

C. A mixture of 3.38 g (0.025 mole) of decahydronaphthalene containing 30% of the cis and 70% of the trans isomer* (b.p. 59.6-62.0° at 10 mm; n_D^{20} 1.4739) and 4.91 g (0.049 mole) of heavy sulfuric acid (4136 γ) was agitated for 11 hours 30 minutes. The value found for the density excess of the combustion water from the decahydronaphthalene was 18 γ, and the value calculated for exchange of all hydrogen atoms was 683 γ.

These results indicate that neither decahydronaphthalene isomer takes part in a hydrogen-exchange reaction.

9. Treatment of a Mixture of Methylcyclohexane and n-Heptane with Heavy Sulfuric Acid. A. A mixture of 0.95 g of methylcyclohexane, 0.82 g of n-heptane, and 5.75 g of heavy sulfuric acid (16,000 γ) was agitated in a sealed tube for 11 hours. The value found for the density excess of the combustion water obtained from the mixture of hydrocarbons was 3674 γ, and the values calculated were 4766 γ for exchange with both hydrocarbons, and 3698 γ for exchange only with methylcyclohexane.

B. A mixture of 0.88 g of methylcyclohexane, 0.76 g of n-heptane, and 4.26 g of heavy sulfuric acid (16,000 γ) was agitated for 50 hours. The value found for the density excess of the combustion water was 3328 γ, and the values calculated were 3317 γ for hydrogen exchange with methylcyclohexane and 4450 γ for exchange with both hydrocarbons.

These results show that only the methylcyclohexane takes part in the exchange reaction.

* The composition of the mixture was determined from the refractive index [7].

We express our deep gratitude for samples of pure hydrocarbons from A. F. Plate (methylcyclopentane and trans-decahydronaphthalene), O. D. Sterligov (cyclohexane, methylcyclohexane, mixture of decahydronaphthalene isomers), and T. F. Bulanova (cyclopentane).

SUMMARY

1. A study has been made of the hydrogen-exchange reaction occurring when heavy sulfuric acid reacts with saturated cyclic hydrocarbons (cyclohexane, methylcyclohexane, 1,1-dimethylcyclohexane, 1,4-dimethylcyclohexane, 1-ethyl-4-methylcyclohexane, cyclopentane, methylcyclopentane, and cis- and trans-decahydronaphthalenes).

2. It has been established that monocyclic hydrocarbons containing tertiary carbon atoms (methylcyclohexane, 1,4-dimethylcyclohexane, 1-ethyl-4-methylcyclohexane, and methylcyclopentane) undergo hydrogen exchange, equilibrium being established in a few hours at room temperature.

3. It has been found that no hydrogen exchange is to be observed between heavy sulfuric acid and cis- and trans-decahydronaphthalenes.

4. It has been established that, when a mixture of a hydrocarbon containing a tertiary carbon atom with a hydrocarbon that does not contain a tertiary carbon atom is treated with heavy sulfuric acid, only the hydrocarbon containing the tertiary carbon atom takes part in hydrogen exchange.

Received January 8, 1953

Institute of Organic Chemistry of the USSR Academy of Sciences

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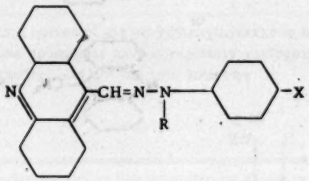
ABSORPTION SPECTRA AND MOLECULAR STRUCTURE

ANALOGOUS BEHAVIOR OF AZO AND IMINO GROUPS

A. A. Kharkharov

It is well known that the replacement in the benzene molecule of $-CH=CH-$ by $-NH-$, $-O-$, or $-S-$ gives heterocyclic compounds that retain properties of aromatic compounds. The present view on the aromatic character of these substances is based on the idea that four electrons from the double bonds and two electrons of the hetero atom form a system that is particularly stable [1, 4]. There is wide acceptance also for the concept of the conjugation of the free electron pairs of the hetero atoms of terminal nucleophilic substituents ($-NR_2$, $-OR$, $-Hal$ etc.) with the π-electrons of aromatic, heterocyclic, and open-chain compounds, as, for example, in aniline, 2-aminopyridine, and acetamide [2, 3, 4].

Recently the concept introduced by Nesmeyanov of the conjugation of single bonds has received general acceptance [4]. We have observed [5] a peculiar case of conjugation in the arylhydrazones of some heterocyclic aldehydes, for example of the type:

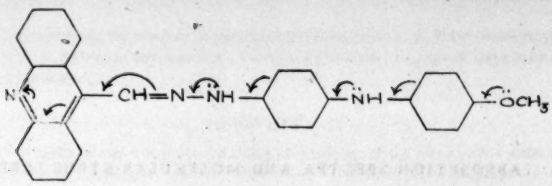


where R = $-H$; $-C_2H_5$, X = $-NO_2$; $-COOH$; $-C(=O)H$; $-SO_3H$; $-H$; $-CH_3$; $-OCH_3$; $-OH$;

$-H$; $-CH_3$; $-OCH_3$; $-OH$; $-NH-C_6H_4-$; $-NH-C_6H_4-COH$, etc.

The peculiarity of systems of this kind is that the acridine nucleus is conjugated with the substituent X via the π-electrons of the $-CH=N-$ group and the benzene ring, which are separated from one another by a group ($-NH-$) that is bound to neighboring atoms by means of two single bonds. The interaction of the π-electrons is here effected with the participitation of the free electron pair of the hetero atom.

The presence of such conjugation in the molecule is indicated, above all, by the color of these compounds. Even the bases of such compounds have intense yellow, orange, or brown colors; and they have characteristic absorption spectra. The position of the maximum of the main absorption band of arylhydrazones of 9-acridinecarboxaldehyde depends on the structure of the substituent (Fig. 1). The hetero atom of the acridine ring system, owing to its electrophilic character, causes a redistribution of electron density in the conjugated chain. In particular, the direction of this redistribution may be shown for the p-(p-anisidinophenyl)hydrazone of 9-acridinecarboxaldehyde (see following page):



The effect of the substituent, as will be seen from the curves given in Fig. 1, is however insufficiently clearly expressed in this case. The bathochromic effect of substituents has a particularly strong influence on the color of salts of these bases. For example, salt formation in the case of the compound cited above (II) is accompanied by displacement of the absorption maximum from 485 to 715 mμ (II and VIII, cf. Fig. 1 and 3), and in the case of the p-nitrophenylhydrazone of 9-acridinecarboxaldehyde (I) – from 444 to 522 mμ (I and VI, Fig. 1 and 3).

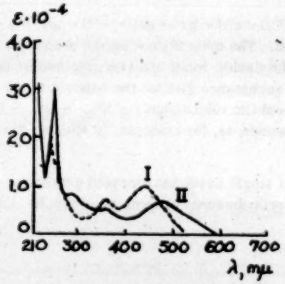
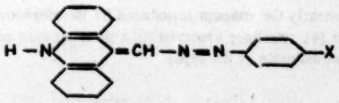


Fig. 1. Absorption spectra in alcoholic solution: ----- p-nitrophenylhydrazone of 9-acridinecarboxaldehyde (I); — p-(p-anisidinophenyl)hydrazone of 9-acridinecarboxaldehyde (II).

The monoacid salts of compounds of this type behave as typical dyes: they are not only intensely colored, but also have the ability to dye textile fibers. These properties can only be possessed by such compounds when the substituent X is conjugated with the acridine ring system. It might be thought that substances of this kind have not the hydrazone, but the azo structure:



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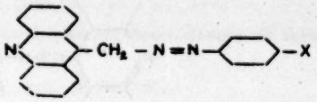
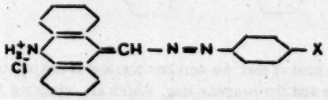


and their salts, correspondingly:



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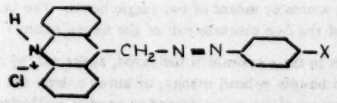


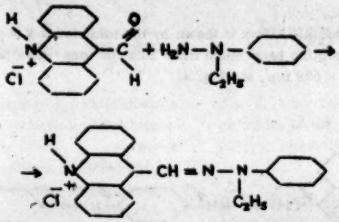
In the first case the nucelophilic group would be conjugated with the long electrophilic chain of alternating double and single bonds, and in the second case we should have a nonconjugated system, in which the electrophilic group would be isolated from the nucleophilic methylene group. The investigations of Izmailsky and coworkers have

shown that some nonconjugated systems of the diphenylmethane type containing electrophilic and nucleophilic substituents in different rings are colored, in spite of the absence of conjugation. However, unlike the compounds cited below, substances of this sort cannot have a very deep color. The color of compounds having nonconjugated systems is not generally deeper than red, and it never attains blue or green.

The bases of the substances that we are describing are also highly colored, but among their salts with acids and bases there are some compounds having absorption maxima almost at the infrared limit of the spectrum (see, for example, Fig. 3; for the substance (VIII), $\lambda_{max} = 715$). The nature of the effect of substituents does not depend on the hydrogen ion concentration.

It is doubtful whether molecular complexes can be stable both in acid and in alkaline media. The main feature, however, distinguishing the nonconjugated systems studied by Izmailsky [6-16] and molecular complexes [16-18] from our compounds is that the former are not dyes having affinity for protein and cellulose fibers. It should be noted that, in accord with the ideas developed in this paper, dyes of the Variamine Blue type must be assigned not to the nonconjugated group, but to the group of systems in which conjugation occurs through $-NH-$.

In order to exclude the possibility of the azo structure, we prepared the ethylphenylhydrazone of 9-acridinecarboxaldehyde, which is incapable of isomerization, by the reaction:



Comparison of the absorption curves of the ethylphenylhydrazone and phenylhydrazone of 9-acridinecarboxaldehyde (Fig. 2) showed that these substances have completely analogous structures. The substances that we have studied, therefore, have the hydrazone, and not the azo, structure.

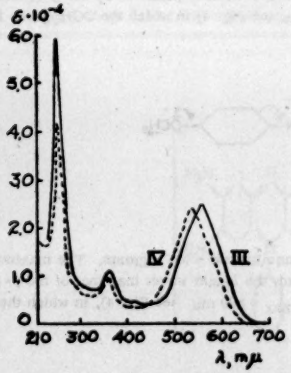


Fig. 2. Absorption spectra of hydrochlorides in alcoholic solution: — phenylhydrazone of 9-acridinecarboxaldehyde (III); ----- ethylphenylhydrazone of 9-acridinecarboxaldehyde (IV).

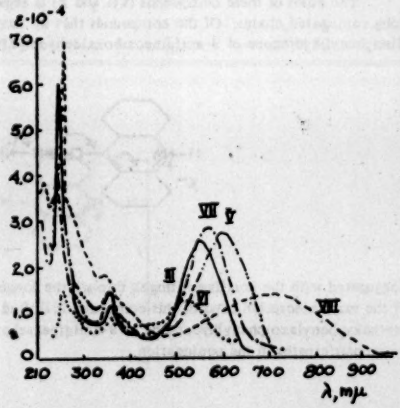
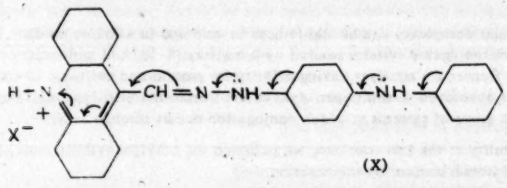


Fig. 3. Absorption spectra of solutions of hydrochlorides in alcoholic HCl: — phenylhydrazone of 9-acridinecarboxaldehyde (III); — ··· — ··· — p-methoxyphenylhydrazone of 9-acridinecarboxaldehyde (V); . . . . p-nitrophenylhydrazone of 9-acridinecarboxaldehyde (hydrochloride of I), (VI); — · · — · · — p-phenylazophenylhydrazone of 9-acridinecarboxaldehyde (VII); —— p-(p-anisidinophenyl)hydrazone of 9-acridinecarboxaldehyde (hydrochloride of II) (VIII)

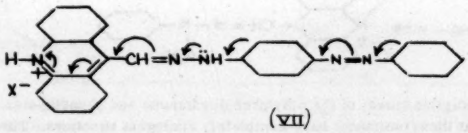
The great deepening of color on passing from the bases of arylhydrazones of 9-acridinecarboxaldehyde to their salts is to be explained as follows: the addition of a proton to the free electron pair of the acridine nitrogen intensifies its electrophilic properties and therefore its influence on the substituent X.

As we have already indicated, the nature of the substituent X in the aromatic nucleus attached through $-NH-$ has a very great influence on the color of the compound (Fig. 3). Thus, when X = H (III), λ_{max} of the main absorption band is 562 mμ; when X = NO_2 (VI), the absorption maximum is displaced towards the shorter waves (λ_{max} = 522 mμ), and when X = OCH_3 (V) it is displaced towards the longer waves (λ_{max} = 610 mμ).



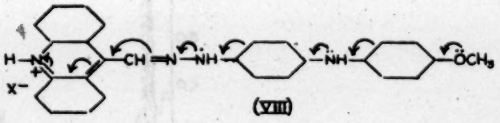
(X)

A particularly powerful bathochromic effect is shown by the substituent X = $-NH-C_6H_5$ (X)[(λ_{max} = 675 mμ, see Fig. 4)]. It displaces the absorption band much more into the long-wave part of the spectrum than the substituent $-N=N-C_6H_5$ (VII) (λ_{max} = 579 mμ, see Fig. 4).



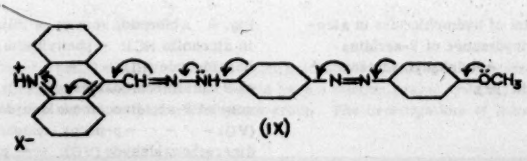
(VII)

The color of these compounds (VII and X) is associated, above all, with the presence in their molecules of long conjugated chains. Of the compounds that we have prepared, the deepest color is possessed by the p-(p-anisidinophenyl)hydrazone of 9-acridinecarboxaldehyde (VIII, λ_{max} = 715 mμ; see Fig. 4) in which the OCH_3 group is



(VIII)

conjugated with the acridine nitrogen through the longest chain, which contains two $-NH-$ groups. The maximum of the main absorption band of this compound is shifted much more towards the longer waves than that of the p-(p-methoxyphenylazo)phenylhydrazone of 9-acridinecarboxaldehyde (IX, λ_{max} = 590 mμ see Fig. 4), in which the azo group participates in the conjugation.



(IX)

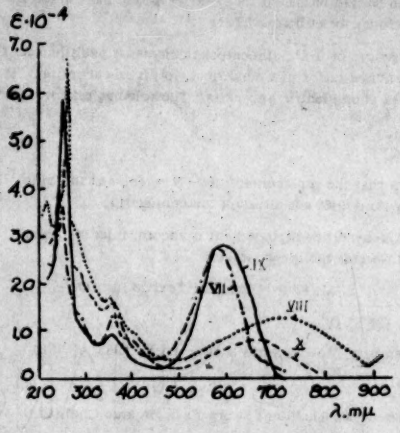


Fig. 4. Absorption spectra of solutions of hydrochlorides in alcoholic HCl: — · — · — p-phenylazophenylhydrazone of 9-acridinecarboxaldehyde (VII); . . . . p-(p-anisidinophenyl)hydrazone of 9-acridinecarboxaldehyde (VIII); — p-(p-methoxyphenylazo)phenylhydrazone of 9-acridinecarboxaldehyde (IX); ---- p-anilinophenylhydrazone of 9-acridinecarboxaldehyde (X).

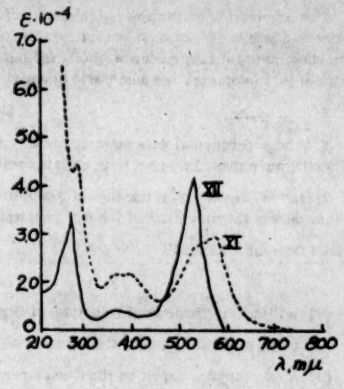
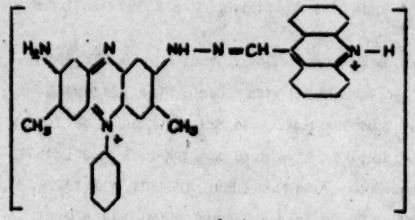


Fig. 5. Absorption spectra of solutions of the hydrochlorides of the compound (XI) and of Safranine T (XII) in alcoholic HCl.

In both cases the introduction of an OCH_3 group has a bathochromic effect. This indicates that in the systems under examination replacement of an azo group by an imino group not only does not interrupt the conjugation of the chain, but even intensifies it. A still more convincing proof that the replacement of an azo or other double-bonded grouping by the imino group does not interrupt the conjugation is provided by the substantive properties of some members of this class of dyes.

A dye that we have prepared (XI, λ_{max} = 570 mμ; see Fig. 5)•:



(XI)

not only has a deeper color than Safranine T (XII, λ_{max} = 535 mμ), but differs from it also in being able to dye cellulose fibers (cotton, viscose and cuprammonium rayons) directly from aqueous solution without the use of a mordant. As Porai-Koshits, Bogoslovsky, and others (19-22] have shown, this property is generally possessed by only

• The author's formula is correctly transcribed, here, although the fact that the dye is compared with Safranine T suggests that the phenyl group should be attached to the other N of the phenazine ring system. —Publisher.

those dyes that contain a long chain of alternating single and double bonds. If the $-NH-$ group interrupted the conjugated chain, then the compound (XI) could not have affinity for cellulose fibers.

The information on the absorption spectra of arylhydrazones of 9-acridinecarboxaldehydes is published for the first time. The dye Safranine, taken for comparison and measured under like conditions, forms an exception. The spectrophotometric measurements were carried out in an SF-1 photoelectric apparatus. The solvents used were a 0.2 N solution of HCl in ethanol and pure (96%) ethanol.

SUMMARY

1. The experimental data presented in this paper show that the replacement of $-N=N-$, and therefore other analogous groups, by $-NH-$ in certain conjugated systems does not interrupt the conjugation.

2. In the case of arylhydrazones of 9-acridinecarboxaldehyde this replacement is accompanied by a considerable shift of the maximum of the main absorption band towards the longer waves.

Received December 28, 1952.

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ISOMERIZATION REACTIONS OF OLEFINIC HYDROCARBONS IN PRESENCE OF ALUMINOSILICATES

COMMUNICATION 2

A. A. Petrov

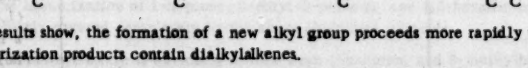
In the preceding communication we examined isomerization reactions of olefinic hydrocarbons, mainly of normal, or only slightly branched, structure [1]. It was shown that, in presence of an aluminosilicate catalyst, olefins of normal structure are readily isomerized to monoalkylalkenes, and in these migration of methyl side groups may occur in the main carbon chain. In order to explain the processes that occur, we made use of M. D. Lvov's hypothesis, according to which intermediate formation of alkylcyclopropanes occurs.

In the present paper we describe the continuation of this investigation, in which we have studied the isomerization of several new types of unsaturated hydrocarbons. We have examined, in particular, the following questions: 1) the possibility of the catalytic synthesis of dialkylalkenes from monoalkylalkenes, the examples taken being branched olefins in which the side methyl group is well removed from the double bond; 2) the stability of a quaternary carbon atom in olefinic hydrocarbons; 3) isomerization of cyclic olefinic hydrocarbons associated with a change in the number of carbon atoms in the ring; 4) disproportionation of carbon atoms of side chains of cyclic olefinic hydrocarbons; 5) confirmation of our previously proposed scheme of isomeric changes in olefins in presence of aluminosilicates, and its elaboration in greater detail by the application of new experimental data. The principal results of our investigation are given in Tables 1 and 2.

The conditions employed were the same as in the previously published work. Whatever hydrocarbon was taken, the products of the catalytic changes were found to consist not only of unsaturated hydrocarbons, but also of saturated hydrocarbons formed by the saturation of olefins in the course of a hydrogen-redistribution reaction. In this investigation our main attention was directed to the structure of the saturated hydrocarbons obtained, but in certain cases we have separated the saturated and unsaturated parts of the catalyzate and studied them separately. The separation of the unsaturated hydrocarbons was effected by hydrogen bromide addition followed by conversion of the products via organomagnesium compounds to saturated hydrocarbons, and for this reason the hydrocarbons corresponding in structure to the unsaturated hydrocarbons of the catalyzate are given in the column headed "unsaturated part" in Table 1.

The results on the isomerization of cyclic olefinic hydrocarbons are given in Table 2. Since the saturation of cyclic olefins by the hydrogen-redistribution reaction proceeds considerably more readily than the saturation of aliphatic olefins, the experimental conditions were somewhat modified for the work on cyclic compounds. Also, only the saturated products, which in these cases formed the main bulk of the catalyzate, were investigated.

We shall now consider the results obtained. The first group of hydrocarbons investigated consisted of olefins in which there was an alkyl side group in a position remote from the double bond. In investigating the isomerization of hydrocarbons of this type, we wished to determine whether it was possible under the selected conditions for a second alkyl group to be formed at the double bond, or whether the double bond would migrate along the carbon chain until an olefin was formed having a tertiary double bond. In other words, according to which of the schemes below would hydrocarbons of this structural type react:



(1); (2).

As the experimental results show, the formation of a new alkyl group proceeds more rapidly than double-bond migration, and the isomerization products contain dialkylalkenes.

It is true that to some extent the double bond of the original hydrocarbon is apparently able to migrate towards the alkyl side group, and may even reach it. This process is indicated by the occurrence of 2-methylalkanes (2-methylpentane, 2-methylhexane, etc.) among the products obtained from hydrocarbons of this type. In general, these 2-methylalkanes can be regarded as saturated forms of the original hydrocarbons, without postulation of the occurrence of any isomeric change, but the frequently observed selective saturation of olefins having tertiary double bonds

TABLE 1

Isomerization Products of Olefins.

Experimental conditions: 250°; space velocity 0.2 liter/liter · hr; duration of experiment 100 minutes

No.	Original hydrocarbon	Composition of catalyzate	
		saturated part	"unsaturated part" (after conversion into saturated hydrocarbons)
1	4-Methyl-1-pentene	2-Methylpentane, 2,3-dimethylbutane	–
2	5-Methyl-1-hexene	2-Methylhexane, 2,4-dimethylpentane; in smaller amount 2,3-dimethylpentane	Composition same as saturated part
3	6-Methyl-1-heptene	2-Methylheptane, 2,5-dimethylhexane; in smaller amounts 2,4- and 2,3-dimethylhexanes	Composition same as saturated part
4	1-Heptene	2-Methylhexane, 3-methylhexane; a little 2,4-dimethylpentane	2-Methylhexane, 3-methylhexane
5	4,4-Dimethyl-1-pentene	2,3-Dimethylpentane, 2-methylhexane	–
6	2,3,3-Trimethyl-1-butene	2,2,3-Trimethylbutane, a little 2,4-dimethylpentane	Various amounts of 2,2,3-trimethylbutane and 2,4-dimethylpentane
7	1,5-Hexadiene	2-Methylpentane, a little 2,3-dimethylbutane	–
8	3-Ethyl-2-pentene	2-Methylhexane, 3-methylhexane, a little 2,4-dimethylpentane	–
9	2-Methyl-2-hexene	2-Methylhexane, 3-methylhexane, 2,4-dimethylpentane	–

NOTE: In the catalyzates from hydrocarbons No. 2 and 5 the presence of a certain amount of 3-methylalkanes was noted.

TABLE 2

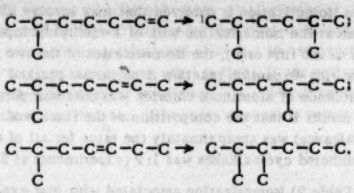
Isomerization Products of Cyclic Olefins

Experimental conditions: space velocity 0.6 liter/liter · hr; duration of experiment 100 minutes

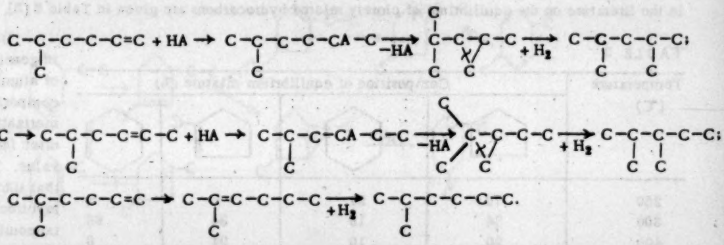
No.	Original hydrocarbon	Composition of catalyzate	
		in experiments at 250°	in experiments at 400°
1	1-Ethylcyclopentene	5-membered cycloalkanes 45%, methylcyclohexane 55%	Methylcyclohexane 27%, toluene 8%, 5-membered cycloalkanes 65% (mainly 1,3-dimethylcyclopentane)
2	1-Ethylcyclohexene	5-membered cycloalkanes 35%, 1,4-dimethylcyclohexane 65%	5-membered cycloalkanes 42%, aromatics 20% (xylenes), 6-membered cycloalkanes 38% (1,4-dimethylcyclohexane, a little 1,3-dimethylcyclohexane)
3	1-Propylcyclohexene	6-membered cycloalkanes 72%, 5-membered cycloalkanes 28%	–
4	Allylcyclohexane	6-membered cycloalkanes 64%, 5-membered cycloalkanes 36%	–
5	Allylbenzene	Monoalkylbenzene	–

under conditions of hydrogen redistribution compels us to postulate a preliminary migration of the double bond in these hydrocarbons. This supposition is supported also by the absence of olefins having a primary-secondary double bond in the products obtained from these same hydrocarbons.

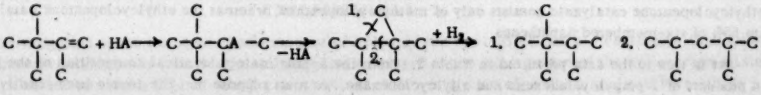
Finally, the occurrence of 2,4- and 2,3-dimethylhexanes in the 6-methyl-1-heptene catalyzate forms a clear proof of the migration of the double bond:



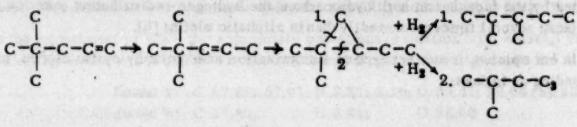
Transformations of hydrocarbons of this type can be expressed by the aid of our proposed mechanism in the following manner*:



The second group of hydrocarbons investigated were olefins having quaternary carbon atoms. In studying the transformations of hydrocarbons of this type, we tried to determine the circumstances under which the very vulnerable grouping at the quaternary carbon could be preserved under the conditions of aluminosilicate catalysis, or, in fact, of acid catalysis in general. Our results show that, when the double bond of the original hydrocarbon is attached to an alkyl side group (tertiary double bond), a quaternary grouping may be preserved. When, however, there is no tertiary double bond in the original hydrocarbon, a quaternary grouping is readily broken down. On the basis of our proposed scheme, the processes occurring may be represented as follows:



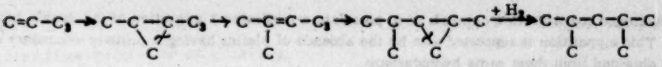
Formation of a certain amount of 2,4-dimethylpentane occurs as a result of rupture of the three-membered ring at the point marked "2". Similarly for 4,4-dimethyl-1-pentene:



We shall not consider the isomerization of 1-heptene, 3-ethyl-2-pentene, and 1,5-hexadiene in detail since their transformations are obviously covered completely by the above-described schemes.

We may add that 2-methylhexane is obviously formed from 1-heptene, and 3-methylhexane from 2-heptene, i.e., completely analogously to the transformations of 5-methyl-1-hexene. It is interesting that a certain amount of 2,4-dimethylpentane is formed from 1-heptene; this is probably formed in accordance with the following scheme:

* HA(HAlSiO$_4$) denotes the aluminosilicate catalyst, which we are regarding as an acid having a hydrogen atom "H" that is capable of undergoing exchange with the hydrogen atoms of hydrocarbons.



The conversion of 3-ethyl-2-pentene into 2-methylhexane probably goes with intermediate formation of 3-methyl-2-hexene.

In the cyclic olefin series isomerization is observed that may involve either expansion or contraction of the ring. It is interesting that, whereas the isomerization both of 1-methylcyclopentene and of 1-methylcyclohexene goes with difficulty (especially in the first case), the isomerization of the two corresponding ethylcycloalkenes goes considerably more readily. The ring-expansion reaction is particular marked in cyclopentanes. A similar readiness for cyclopentanes to react in presence of aluminum chloride was observed previously by Zelinsky and coworkers [2]. A characteristic feature of our results is that the composition of the final products (with respect to the content of five- and six-membered cycloalkanes) was approximately the same for all of the original hydrocarbons. The approximate ratio of five- and six-membered cycloalkanes was 1:2 (experiments at 250°).

At higher temperatures (Table 2) isomerization associated with ring expansion in cyclopentenes fell appreciably, a fact that is in general accord with the high stability of five-membered naphthenes at high temperatures. The data in the literature on the equilibrium of closely related hydrocarbons are given in Table 3 [3].

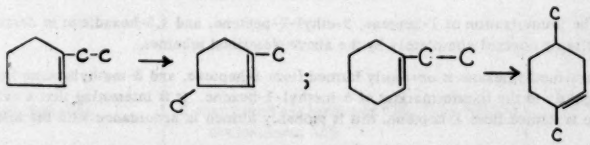
TABLE 3

Temperature (°C)	Composition of equilibrium mixture (%)			
250	79	21	—	—
300	84	16	34	66
400	90	10	94	6

It must be pointed out that in general, under the conditions of aluminisilicate catalysis, the composition of the mixture of isomerization products obtained is often far from the equilibrium value. This arises from the fact that the hydrogen-redistribution reaction that is proceeding simultaneously effects considerable changes in the composition of the isomerization product, saturating one or another form of hydrocarbon preferentially. This circumstance assumes even greater importance when we consider that paraffins and cycloparaffins are chemically inert under these conditions. The most characteristic example is found in a comparison of the isomerization of 1-methylcyclopentene and of 1-ethylcyclopentene. Since the six-membered isomer of the first hydrocarbon (cyclohexene) has a secondary double bond, and the corresponding isomer of the second hydrocarbon (methylcyclohexene) has a tertiary double bond, and since, under the conditions of aluminosilicate catalysis, hydrocarbons having tertiary double bonds are selectively saturated, it is found that the methylcyclopentene catalyzate consists only of methylcyclopentane, whereas the ethylcyclopentene catalyzate contains 55% of six-membered naphthenes.

Let us turn to the data presented in Table 2. From the approximately identical composition of the isomerization products of 1-propylcyclohexene and allylcyclohexane, we must suppose that the double bond readily migrates from the side chain to the ring. Similar ready migration of the double bond of allylcyclohexane in presence of a platinum catalyst has been noted previously by Levina [4]. Another proof of the formation of 1-propylcyclohexene from allylcyclohexane is afforded by the fact that in both hydrocarbons the hydrogen-redistribution reaction proceeds with approximately equal readiness; several times more readily than in aliphatic olefins [5].

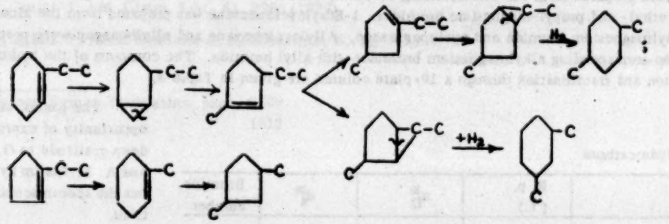
Of still greater interest, in our opinion, is another type of isomerization undergone by cyclic olefins, namely redistribution of radicals, proceeding as follows:



We have found that 1-ethylcyclohexene and, to a lesser extent, 1-ethylcyclopentene show this type of isomerization. A paper has recently appeared in which it is shown that isomerization of a similar type is undergone by isopropylcyclo-

hexene in presence of alumina impregnated in HCl [6]. In our experiments this sort of isomerization occurred very readily at 250° and at 400°.

In particular, all of the six-membered naphthenes of the 1-ethylcyclohexene catalyzate consisted of dimethylcyclohexanes. It is interesting that at 250° the sole isomerization product was 1,4-dimethylcyclohexane, and only in the 400° experiment was a comparatively small amount (20%) of 1,3-dimethylcyclohexane found. What is the mechanism of these transformations? Of the two possible schemes: a) alkylation of the ring by methyl radicals formed at the expense of the side chain, and b) several successive reactions involving ring formation, preference must be given to the second. Alkylation at atmospheric pressure and at such a low temperature (250°) for an aluminosilicate catalyst, requiring, moreover, the breakdown of an ethyl radical, is not very probable, all the more so since allylbenzene yields only monoalkylbenzene under these conditions, i.e., no redistribution of radicals occurs in a hydrocarbon that is, in general, much more readily alkylated. The most reasonable representation of isomerization of this type is as follows:



These schemes of ring transformations are very probable ones, for the individual stages are in themselves quite reasonable, and the experimental data (see Table 2) are in general agreement. The overall result is that we obtain the most stable forms of cyclopentene or cyclohexene hydrocarbons for the given conditions.

EXPERIMENTAL

Our investigation of the isomeric transformations of hydrocarbons was carried out in a continuous-flow system. The experimental conditions and the analytical procedure employed in the examination of the hydrocarbon mixtures have been published previously [1]. We shall give details of the investigation of products analyzed by methods different from those previously described; the products mainly concerned are those obtained from 1-ethylcyclohexene, which were analyzed by the oxidation of the dehydrogenated (in presence of platinized charcoal) C_8 fraction of the catalyzate. The oxidation was performed under the conditions described by Isagulyants and Egorova [7].

In the experiment at 250°, the appropriate operations (oxidation with $KMnO_4$) yielded crystals that sublimed without melting at above 240°. The elementary composition of these corresponded to that of the phthalic acids:

Found %: C 57.82; 57.67; H 3.77; 3.69; O 39.41; 39.64 (by difference)
Calculated %: C 57.85; H 3.64; O 38.53

The substance was boiled with methanol saturated with HCl (5%) and so converted into the dimethyl ester, which corresponded in melting point (139°) to dimethyl terephthalate.

In the experiment at 400° the same operations yielded crystals that again sublimed without melting and corresponded to the phthalic acids in elementary analysis:

Found %: C 57.88; 57.79; H 3.70; 3.63; O 39.42; 39.58 (by difference)

The methyl esters obtained melted over a wide range (120-139°), but the greater part of the product, obtained by recrystallization from ether, melted at 139°. By making use of the different solubilities of isophthalic and terephthalic acids in alcohol, we showed that our product contained about 70% of terephthalic acid. It was established

by the same method that oxidation of the saturated transformation products of allylbenzene yielded only benzoic acid (m.p. 123°).

The structures of the transformation products of the aliphatic hydrocarbons, and also of the five-membered cycloalkanes of the 1-ethylcyclopentene catalyzate, were established with the aid of Raman spectra.

The hydrocarbons required were obtained synthetically: by the Grignard reaction followed by dehydration of the tertiary alcohols by distillation with iodine, or by the Grignard-Würtz reaction, according to the procedure developed by Kazansky and coworkers [8]. 4-Methyl-1-pentene was prepared by the condensation of isopropylmagnesium bromide with allyl bromide. 1,5-Hexadiene was prepared by Cortes' method from allyl bromide [9]. 5-Methyl-1-hexene was prepared by the condensation of isobutylmagnesium bromide and allyl chloride, and 1-heptene from butylmagnesium bromide and allyl bromide. 4,4-Dimethyl-1-pentene was prepared by the action of allyl chloride on tert-butylmagnesium chloride. 3-Ethyl-2-pentene was prepared from 1,1-diethyl-1-propanol, prepared by the Grignard method from ethylmagnesium bromide and propionic ester. 2,3,3-Trimethyl-1-butene was prepared from 1,1,2,2-tetramethyl-1-propanol, obtained from methylmagnesium iodide and pinacolone. 6-Methyl-1-heptene was prepared by the condensation of isopentylmagnesium bromide and allyl bromide. 1-Ethylcyclohexene and 1-propylcyclohexene were prepared from the corresponding alcohols, which were obtained by the Grignard method from cyclohexanone and ethyl- and propyl-magnesium bromides. 1-Ethylcyclopentene was prepared from the alcohol synthesized from ethylmagnesium bromide and cyclopentanone. Allylcyclohexane and allylbenzene were prepared by condensation of the corresponding alkylmagnesium bromides with allyl bromide. The constants of the hydrocarbons, after purification and fractionation through a 10-plate column are given in Table 4.

TABLE 4

Constants of Hydrocarbons

Hydrocarbon	B. p. (°C)	n_D^{20}	d_4^{20}	Bromine number
4-Methyl-1-pentene	53-54	1.3820	0.6683	185
1,5-Hexadiene	59-60	1.4040	0.6845	391
5-Methyl-1-hexene	84-85	1.3965	0.6926	165
1-Heptene	93-94	1.4000	0.7031	160
2-Methyl-2(1)-hexene	91-95	1.4070	0.7053	162
3-Ethyl-2-pentene	93-95	1.4150	0.7210	167
4,4-Dimethyl-1-pentene	71-72	1.3925	0.6991	162
2,3,3-Trimethyl-1-butene	77-79	1.4025	0.7060	164
6-Methyl-1-heptene	112-114	1.4065	0.7121	142
1-Ethylcyclopentene	104-106	1.4420	0.7989	179
1-Ethylcyclohexene	134-136	1.4566	0.8290	141
1-Propylcyclohexene	150-152	1.4580	0.8410	110
Allylcyclohexane	148-151	1.4507	0.8088	118
Allylbenzene	157-159	1.5112	0.8930	134

The author takes this opportunity of expressing his deep gratitude to G. D. Gal'pern and A. N. Kislitsky for carrying out the spectroscopic investigations.

SUMMARY

1. In presence of an aluminosilicate catalyst at 250°, acyclic and cyclic olefin hydrocarbons undergo considerable structural changes, which are readily explained by means of a mechanism scheme in which the intermediate formation of cyclopropane derivatives is postulated. The following are the most characteristic types of isomeric transformations: 1) isomerization of normal olefins into monoalkylalkenes in which the alkyl group stands at the double bond; 2) formation of dialkylalkenes from monoalkylalkenes in which the alkyl side group is well removed from the double bond; 3) breakdown of a grouping at a quaternary carbon atom, except in those cases in which, in addition to a quaternary carbon, there is a tertiary carbon at the double bond; 4) in the isomerization of C_7 (and higher) cycloalkenes, a mixture of two parts of six-membered and one part of five-membered naphthenes is formed; 5) in hydrocarbons having a primary-secondary double bond, migration of the double bond so as to form unsymmetrically substituted ethylene derivatives readily occurs; 6) reduction in the number of carbon atoms in alkyl side groups occurs.

2. The overall result of the catalytic transformations of olefinic hydrocarbons in presence of aluminosilicate should be regarded as the summative effect of isomerization and hydrogen-redistribution processes, and the unsaturated hydrocarbons that are mainly formed are those which have the least tendency to undergo isomerization under the experimental conditions and which are readily saturated at a later stage owing to the redistribution of hydrogen. The most characteristic forms of saturated C_6—C_8 hydrocarbons obtained at 250° we consider to be: 2-methylalkanes; 2,3-, 2,4-, and 2,5-dimethylalkanes; methylcyclopentane; methylcyclohexane; and also 1,3-dimethylcyclopentane and 1,4-dimethylcyclohexane.

Received February 13, 1953

Petroleum Institute of the USSR
Academy of Sciences

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CONDUCTIVITY OF ACID CATALYSTS; AND ITS VARIATION DURING ALKYLATION AND POLYMERIZATION REACTIONS

Ya. M. Paushkin and M. V. Kurashev

One of the funadmental properties of acid catalysts is the electrical conductivity associated with the ionic character of acids. According to modern views, acid catalysis is to be explained by the ability of acids to dissociate into ions, which take part in the intermediate stages of the reaction. The mechanism of alkylation (I) and polymerization (II) with the participation of protons may be represented by the following scheme [1]:

$$(CH_3)_2C{=}CH_2 + H^+ \longrightarrow (CH_3)_3C^{\oplus} \xrightarrow{C_4H_8} C_8H_{17}^{\oplus} \begin{cases} \xrightarrow{i\,C_4H_{10}} C_8H_{18} + (CH_3)_3C^+ & \text{(I)} \\ \xrightarrow[C_4H_8]{} C_8H_{16} + H^+ & \text{(II)} \end{cases}$$

Reaction is initiated by addition of a proton at a double bond, which leads to the formation of a tert-butyl carbonium ion. This carbonium ion then adds to 2-methylpropene with formation of a C_8H_{17} carbonium ion, which, depending on the reaction conditions, may be converted in presence of isobutane into an octane isomer and a carbonium ion (alkylation), or may be converted into an octene isomer (polymerization) with elimination of a proton.

In connection with the participation of ions in the reaction, it is of interest to investigate the conductivity of acid catalysts as a supplementary physicochemical parameter that gives an indication of the variation of the properties of the catalyst, particularly its ionic character, in the course of the reaction. Volkenshtein [2] points out that catalytic activity, like conductivity, must be assigned to the category of "structure-sensitive" properties of heterogeneous catalysts. There is a relationship between the catalytic activity of a semiconductor and its conductivity, i.e., between the rate constant for the reaction and the conductivity of the catalyst κ at a given temperature, and it may be represented by the function:

$$k_T = k\varphi(\kappa_T).$$

The conductivity can serve as a characteristic of the activity only insofar as we are concerned with various samples of the same catalyst differing in the content of an additive that does not affect the general nature of the catalyst. The specific conductivity of liquid electrolytes is determined by the concentration of ions and their mobility:

$$\kappa = c(u + v),$$

in which κ is the specific conductivity, c is the ionic concentration, and u and v are the ionic mobilities, i.e., the product of charge and velocity. The mobility of the hydrogen ion is 313 coulomb·cm/sec, and those of the ions F^-, NO_3^-, and $\frac{1}{4}SO_4^-$ vary over the range 46.6-67 coulomb·cm/sec.

For heterogeneous catalysts a direct relationship has been established purely theoretically between catalytic activity and the conductivity of the catalyst. If acid catalysis were due directly to free protons, it would be possible to find a relationship between conductivity and catalytic activity.

As will be seen below, however, no general relationship is to be observed between the conductivity and activity of acid catalysts. This may be explained by the fact that protons are not met in the free state in anhydrous acids, but are combined in the form of complex ions of the type $[H_2X]^+$. The formation of a carbonium ion may, therefore, be associated with two successive stages: elimination of a proton from complex ion, $[H_2F]^+$, $[H_2SO_4]^+$, or $[H_4PO_4]^+$, and its addition to a double bond. The tendency for protons to be eliminated is not identical for different ions and may not be related to the conductivity.

The catalytic activity is most fully expressed by Hammett's function [3], which is determined with the aid of indicators and characterizes the tendency for an acid catalyst to lose a proton when a proton acceptor appears. Since this method is associated with the use of colored indicators, it is suitable only for uncolored media.

In the present investigation we have studied the conductivity of a number of acid catalysts in relation to their catalytic activities, and we have studied also the variation of conductivity in the course of alkylation and polymerization reactions. Apart from the usual alkylation and polymerization catalysts, the compounds of boron trifluoride, which comprise a large group of catalysts, are of great interest. The most interesting of these are the strong complex acids, such as $BF_3 \cdot H_2O$; $BF_3 \cdot 2H_2O$; $HF \cdot H_2O \cdot BF_3$; $H_3PO_4 \cdot BF_3$.

A number of papers has appeared recently on the electrochemistry of boron trifluoride compounds. The material published on this question is, however, very limited in scope, and is concerned with only a few compounds. Thus, up to 1950 the conductivity was known for only five boron trifluoride compounds [4]:

Compound	Conductivity at 25°	
$(C_2H_5)O \cdot BF_3$	$\kappa = 2{,}97 \cdot 10^{-4}$ ohm$^{-1} \cdot$ cm^{-1}	[4]
$BF_3 \cdot H_2O$	$\kappa = 42{,}0 \cdot 10^{-3}$ ohm$^{-1} \cdot$ cm^{-1}	[4]
$BF_3 \cdot 2H_2O$	$\kappa = 105{,}0 \cdot 10^{-3}$ ohm$^{-1} \cdot$ cm^{-1}	[5]
$BF_3 \cdot 2CH_3OH$	$\kappa = 22 \cdot 10^{-3}$ ohm$^{-1} \cdot$ cm^{-1}	[4]
$BF_3 \cdot 2C_6H_5OH$	$\kappa = 1{,}1 \cdot 10^{-3}$ ohm$^{-1} \cdot$ cm^{-1}	[6]
BF_3 liquid at −120°	$\kappa = 5 \cdot 10^{-10}$ ohm$^{-1} \cdot$ cm^{-1}	[7]

The conductivity of the etherate of boron trifluoride has been investigated over the range −9.4° to +44.7° [4], its extreme values being $1{,}344 \cdot 10^{-4}$ and $4{,}58 \cdot 10^{-4}$ ohm$^{-1} \cdot$ cm^{-1} respectively. The conductivity of boron trifluoride dihydrate $BF_3 \cdot 2H_2O$ varies from $4{,}81 \cdot 10^{-2}$ to $10{,}52 \cdot 10^{-2}$ ohm$^{-1} \cdot$ cm^{-1} over the range + 2.6 −45.5° [8]. Conductivity varies linearly with temperature.

A paper has been published recently by Sklyarenko [9] on the determination of the conductivity and other physicochemical properties of orthophosphoric acid at various concentrations at 25°.

Concentration of H_3PO_4 (%)	Density (g/cc)	Specific conductivity (ohm$^{-1} \cdot$ cm^{-1})
81,39	2,6401	0,09916
88,22	1,7242	0,07466
93,10	1,7886	0,06150
97,35	1,8443	0,05093

For sulfuric acid at concentrations of 80, 90, and 100% at 18°, conductivity values of 0.110, 0.107, and 0.0157 ohm$^{-1} \cdot$ cm^{-1} respectively are cited.

The investigation of the conductivity of a few BF_3 compounds has made it possible to elucidate the structure of boron trifluoride compounds [10]. Thus, the high conductivity of boron trifluoride hydrates shows that they are strong acids of the type of trifluorhydroxyboric acid $H^+[HO:BF_3]$ and the hydrate of this acid $H_3O^+[HO:BF_3]$. The ethyl-etherate of boron trifluoride has a considerably greater conductivity ($2{,}97 \cdot 10^{-4}$ ohm$^{-1} \cdot$ cm^{-1}) than those of the original ether ($3 \cdot 10^{-13}$ ohm$^{-1} \cdot$ cm^{-1}) and liquid BF_3 ($5 \cdot 10^{-10}$ ohm$^{-1} \cdot$ cm^{-1}), thus indicating the appreciable ionization of the etherate molecule. Electrolysis of the ethyl-etherate is accompanied by evolution of hydrogen and ethane. On this basis we can regard the etherate of boron trifluoride as an ethyl derivative of trifluoroethoxyboric acid $C_2H_5^+[C_2H_5O:BF_3]$, the ionization of which is less marked than that of the acid itself [4].

EXPERIMENTAL

The conductivity of the acid catalysts was determined by the usual method with an apparatus consisting of an alternating-current sound generator GZ-1, a resistance box R-14, a drum slide wire, and a vessel containing platinum electrodes. In determining the conductivity, the catalyst (5-6 ml) was placed in a beaker, which was kept in a thermostat to acquire the required temperature. The platinum electrodes were then lowered into the electrolyte, and the conductivity was measured. Several determinations of the conductance were made, and on the basis of these the specific conductivity was calculated by the formula $\kappa = c \cdot k$, in which c is the cell constant and k is the conductance. Below we give the conductivities of a number of acid catalysts, according to the authors' determinations, and also information on the catalytic activity of the catalysts in alkylation and polymerization reactions.

Although acid catalysts are not completely chemically pure substances, since they cannot be distilled or purified by known methods, different samples of the same catalyst prepared at different times were found to have conductivities of the same order. In Table 1 a systematic scheme is given showing the activities and conductivities of a number of catalysts.

TABLE 1

Conductivities and Activities of some Catalysts *

No.	Catalyst	Conductivity at 25° (ohm^{-1}·cm^{-1})			Alkylation of isobutane, isopentane, olefins **			Polymerization at atm. press. and 100° **		
		specific	equiv.	molar	C_2H_4	C_3H_6	C_4H_8	C_2H_4	C_3H_6	1-C_4H_8
1	HF	–	–	–	0	+	+	0	+	+
2	$H_3PO_4 \cdot BF_3$	0.00722	0.205	0.615	+	+	+	Weak	+	+
3	$H_4P_2O_7 \cdot 2BF_3$	0.0067	0.270	1.080	+	+	+	Weak	+	+
4	$BF_3 \cdot H_2O$	0.0386	0.940	1.880	+	+	+	–	+	+
5	$BF_3 \cdot 2H_2O$	0.1660	–	–	0	0	0	0	0	+
6	$CH_3OH \cdot BF_3$	0.01371	0.966	–	0	Weak	+	–	–	–
7	$C_2H_5OH \cdot BF_3$	0.00854	0.718	–	0	Weak	+	0	–	–
8	$C_6H_5OH \cdot BF_3$	0.00053	–	–	0	0	0	0	+	+
9	$(C_2H_5)_2O \cdot BF_3$	0.0003	–	–	0	0	0	0	0	+
10	$H_2SO_4 + BF_3$	0.03569	–	–	+	+	+	–	+	+
11	H_2SO_4	0.03569	1.158	2.316	0	Weak	+	0	Weak	+
12	H_3PO_4	0.0510	0.885	2.66	0	0	0	0	0	+

* The preparation of the catalysts and their properties are given elsewhere [10, 11].

** The sign + indicates that the reaction goes, and the sign 0 indicates that it does not.

No general relation is to be observed between conductivity and catalytic activity. Strong acids, which are active catalysts, have in a number of cases a lower conductivity than less active catalysts.

We give below a table showing the variation of conductivity with temperature for some of the principal catalysts.

TABLE 2

Variation of Conductivity with Temperature

Temperature (°C)	Specific conductivity (ohm^{-1}·cm^{-1})			
	H_2SO_4 (100.1%)	H_2SO_4 (100.1%) + BF_3	$H_3PO_4 \cdot BF_3$	H_3PO_4
0	–	–	0.003207	–
5	0.022005	0.017147	0.004357	–
10	0.029177	0.020119	0.004592	–
15	–	0.025250	0.005209	–
20	0.033685	0.027058	0.005834	–
25	0.043595	0.035694	0.007227	0.0510
30	0.049742	0.041639	0.008108	–

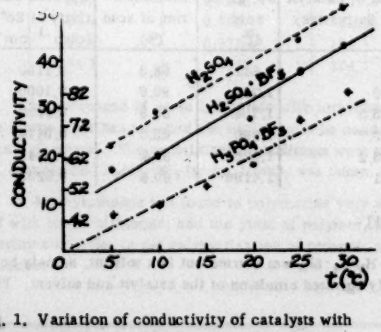

Fig. 1. Variation of conductivity of catalysts with temperature.

Conductivity varies linearly with temperature (Fig. 1).

A study was made of the variation of the conductivity during polymerization and alkylation reactions. For these reactions we took chemically pure benzene, isopentane, and olefins (propene and 2-methylpropene), which were prepared by the dehydration of the corresponding alcohols (olefin content of the gas 98-99%). A number of successive experiments were carried out, and after each of these we determined the yield of polymers or alkyl derivative, the density, conductivity, and catalyst concentration.

Variation in Conductivity in the Alkylation of Benzene with Propene. Successive experiments were carried out on the alkylation of benzene with propene at 15° and atmospheric pressure. For each experiment we took 200 ml of benzene, 30.5 liters of propene (molar ratio 2.75:1), and 25 ml of catalyst, which took part in a number of successive experiments.

After each experiment the reaction product, which consisted of isopropyl benzene (b.p. about 152°) and polyisopropylbenzenes, was fractionated, and the yield of alkyl derivatives boiling above 120° was determined on the basis of the propene taken. The alkylation procedure has already been given in detail by the authors [11]. The results of the experiments are given in Table 3.

TABLE 3

Variation of yield, consumption and properties of $H_3PO_4 \cdot BF_3$ catalyst in the alkylation of propylbenzenes

No.	Yield of alkyl deriv. based on propene (b.p. above 120°)	Catalyst consumption (% on alkyl deriv. obtained)	Sp. gr. of catalyst	Spec. conductivity at 25° ($ohm^{-1} \cdot cm^{-1}$)
0	–	–	1.900	0.00722
1	186	46.2	1.823	0.00647
2	220	21.4	1.816	0.00624
3	236	13.9	1.812	0.00618
4	260	2.9	1.625	0.00535
5	130	8.5	1.331	0.00058

During the reaction the catalyst concentration falls as a result of the dissolution of unsaturated hydrocarbons, and this is shown by a fall in specific gravity and conductivity. At a certain point the activity of the catalyst falls sharply (the yield falls), and this point corresponds to a sharp fall in the conductivity and specific gravity of the catalyst. The graph in Fig. 2 shows the variation in the specific conductivity of the catalyst in the course of reactions carried out in a series of successive experiments with one portion of catalyst.

Variation in Conductivity in the Alkylation of Isopentane with 2-Methylpropene. The alkylation of isopentane with 2-methylpropene was carried out in presence of 98.5% sulfuric acid. 2-Methylpropene (5 liters) was passed into a vigorously agitated mixture of 50 ml of isopentane and 30 ml of sulfuric acid at 10°. The hydrocarbon layer was then distilled, yielding alkyl derivatives boiling in the range 30-170° and a residue boiling above 170°. The results of the experiments are given in Table 4.

Change in the catalyst activity during the alkylation reaction is accompanied by change in conductivity, and the conductivity of the catalyst can, therefore, serve as a supplementary characteristic of the alkylation process.

Conductivity of Sulfuric Acid in the Polymerization of Propene and 2-Methylpropene. Alkylation is always accompanied to some extent by polymerization, and in a number of cases polymerization can be considered as an independent process, so that the study of the conductivity of catalysts in relation to the polymerization process is of undoubted interest.

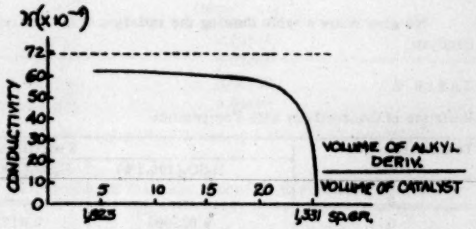

Fig. 2. Variation of conductivity of catalyst in the course of reaction.

TABLE 4

Variation of Yield, and of the Consumption and Properties of Sulfuric Acid, for the Alkylation of Isopentane with 2-Methylpropene*

Expt. No.	Yield of alkyl derivative (% on 2-methylpropene)		Sp. gr. of alkyl deriv. d_4^{20}	Consumption of catalyst (% on alkyl derivative)	Sp. gr. of acid d_4^{20}	Concentration of acid (%)	Specific conductivity at 25° ($ohm^{-1} \cdot cm^{-1}$)
	at 30-170°	above 170°					
0	–	–	–	0	1.842	98.3	0.1150
3	183	28	0.708	209	1.766	90.0	0.1000
4	162	58	0.710	85.5	1.734	86.9	0.0930
6	82	82	0.729	83.7	1.690	83.0	0.0674
7	20	105	0.746	53.2	1.625	62.6	0.0341
8	12.5	42	0.760	51	1.4190	60.6	0.0233

* The authors have already given details of the procedure [11].

The polymerization of olefins in presence of H_2SO_4 and $H_3PO_4 \cdot BF_3$ was carried out in a solvent, namely heptane. Propene or 2-methylpropene was passed into a vigorously agitated emulsion of the catalyst and solvent. The

reaction was carried out at 20-25°, the rate of passage of gas being 1-1.5 liter/hour. After each experiment, in the course of which 4-5 liters of gas was passed, the hydrocarbon layer was separated from the acid layer, washed, and dried. The heptane (b.p. 98.4°) was distilled off up to a temperature of 100°, since the polymers obtained under these conditions boil above 100°. After each experiment the conductivity, titratable acidity, and specific gravity of the catalyst were determined. The polymers were not specially investigated, since this question has been examined in previous investigations [11].

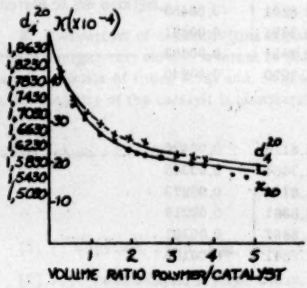

Fig. 3. Variation of conductivity and specific gravity in the polymerization of 2-methylpropene.

The polymerization of propene in presence of sulfuric acid did not proceed very rapidly: a large part of the propene dissolved in the acid, leading to rapid increase in the volume of the acid layer, fall in the acid concentration, and fall in its conductivity, so that polymerization ceased. Under similar conditions 2-methylpropene polymerized readily, and the concentration and conductivity of the acid fell only slowly: over a series of experiments the yield did not change appreciably. The results of the experiments are given in Table 5.

In Fig. 3 a comparison is made of the variations of the conductivity of the catalyst H_2SO_4 in the polymerization of propene and 2-methylpropene, and in the alkylation of 2-methylpropene. In the course of polymerization the electrochemical properties of the catalyst change greatly, but in the course of alkylation the change in the catalyst is slow. Introduction of a substance capable of being alkylated into the reaction raises the stability of sulfuric acid when it reacts with olefins. A polymerization side reaction during alkylation will, therefore, encourage poisoning of the catalyst.

TABLE 5

Variation in the Properties of an H_2SO_4 Catalyst during the Polymerization of Propene and 2-Methylpropene

Expt. No.	Yield of polymer (%)	Sp. gr. of polymer d_4^{20}	Catalyst			Change in conductivity ($ohm^{-1} \cdot cm^{-1}$)
			Consumption (%)	Sp. gr. d_4^{20}	Concentration (%)	
			Propene			
0	–	–	–	1.8351	93.5	0.10773
1	20.8	0.7450	3200	–	–	0.08644
2	15.0	0.7533	1835	1.6393	–	0.05823
4	11.4	0.7644	1106	1.3500	60.9	0.01620
6	4.2	0.7688	890	1.3327	40.3	0.00411
8	Traces	–	–	1.2700	20.4	0.00148
			2-Methylpropene			
1	83.6	0.7460	2100	1.8039	92.0	0.09802
2	66.4	0.7464	654.1	1.7180	86.1	0.07694
5	65.8	0.7852	341.1	1.6254	78.4	0.05358
7	66.4	0.7926	222.4	1.5554	68.9	0.03559
9	95.4	0.7734	154.7	1.5156	67.6	0.02506
10	74.3	0.8012	104.1	1.4220	60.1	0.01920

The compound of boron trifluoride with orthophosphoric acid is one of the most active polymerization catalysts known. We have studied the variation in its conductivity in the course of the polymerization of propene and 2-methylpropene. The experimental conditions were similar to those of the preceding experiment; 30 ml of catalyst, composition $H_3PO_4 \cdot BF_3$ (sp.gr. 1.906), was taken.

2-Methylpropene was found to polymerize very readily in presence of the complex formed by orthophosphoric acid with boron trifluoride, and the yield of polymer, therefore, remained practically unchanged during 15 successive experiments. Also, in the polymerization of propene, the catalyst remained active up to the end of the series of experiments.

TABLE 6

Variation in the Properties of a $H_3PO_4 \cdot BF_3$ Catalyst during the Polymerization of Propene and 2-Methylpropene

Expt. No.	Yield of polymer (%)	Sp. gr. of polymer d_4^{20}	Catalyst		Change in conductivity ($ohm^{-1} \cdot cm^{-1}$)
			Consumption (%)	Sp. gr.	
			Propene		
0	–	–	–	1.903	0.00520
2	81.3	0.7870	728	1.8201	0.00450
4	81.5	0.7951	360	1.7884	0.00421
6	95.0	0.7844	241	1.7831	0.00403
8	70.4	0.7824	187	1.7020	0.00240
			2-Methylpropene		
1	62.9	0.8119	866.7	1.8118	0.00427
2	74.6	0.8001	418.6	1.7464	0.00345
4	89.5	0.8050	190.0	1.6781	0.00273
7	95	0.8010	99.2	1.6361	0.00218
11	85.6	0.8156	61.1	1.5897	0.00197
15	70.1	0.8374	45.6	1.5641	0.00189

An interesting picture is presented when a comparison is made of the variations in the conductivity of the catalyst $H_3PO_4 \cdot BF_3$ in the polymerization of propene and 2-methylpropene and the alkylation of benzene (see Fig. 4). This picture is similar to that observed for sulfuric acid: the catalyst changes little during polymerization, although it is one of the most active polymerization catalysts.

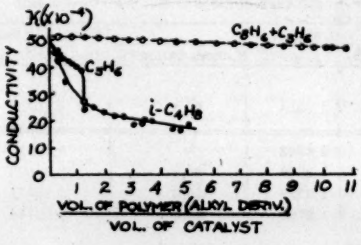

Fig. 4. Variation of the conductivity of $H_3PO_4 \cdot BF_3$ in alkylation and polymerization processes.

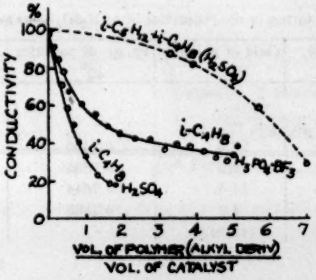

Fig. 5. Variation of the conductivity of catalysts during polymerization and alkylation.

Fig. 5 shows the variation of the conductivity (as percentage of initial value) of sulfuric acid and the complex of orthophosphoric acid with boron trifluoride in the course of the polymerization of 2-methylpropene and of the alkylation of isopentane with 2-methylpropene. The most marked change in conductivity in the course of reaction is observed for sulfuric acid. The conductivity of the catalysts changes rapdily during polymerization, and slowly during alkylation.

The lowering of the catalytic activity and conductivity of catalysts during the polymerization and alkylation of hydrocarbons is to be explained by the formation in the catalyst of partial and full esters, which have low conductivity and do not facilitate ionization. There is, consequently, a reduction in the concentration of the principal substance responsible for the conduction of the current and the promotion of catalysis. For this reason a definite relationship is to be observed between the degree of catalysis and the value of the conductivity, so long as no water is allowed to enter the reaction mixture.

SUMMARY

1. The conductivities of a number of acid catalysts have been investigated, tabulated, and compared with the catalytic activities of these substances.

2. No general relationship is to be observed between the catalytic activity and conductivity when a number of different catalysts are considered, but when one particular catalyst is under consideration, the conductivity forms an index of the activity of the catalyst. The conductivity falls parallel to the specific gravity and titratable concentration of the catalyst.

3. Comparison of conductivities in polymerization and alkylation reactions shows that in alkylation the conductivity changes very slowly, whereas in polymerization it changes very rapidly. Although the alkylation reaction occurs in presence of strong acids and, in general, with a smaller group of catalysts than the polymerization reaction, the stability of the catalyst is considerably higher in alkylation than in polymerization.

Received February 23, 1953

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STUDY OF THE EFFECT OF PRESSURE ON THE POLYCONDENSATION OF THE METHYL ESTER OF GLYCINE

A. M. Polyakova, L. F. Vereshchagin, A. A. Sakharova, and E. S. Tambovtseva

The present investigation forms a continuation of the work of Polyakova and Vereshchagin on the effect of pressure on the hydrolysis of 2,5-piperazinedione and the formation of polypeptide linkages [1]. The authors showed that increase of pressure greatly increases the rate of hydrolysis of 2,5-piperazinedione. Also, it was found that the final reaction mixture consisted not only of liquid hydrolyzate, but contained also a solid water-insoluble product. It was considered that the solid compound was a polypeptide formed from residues of hydrolyzed 2,5-piperazinedione.

Increase in pressure, therefore, not only leads to increase in the rate of hydrolysis of 2,5-piperazinedione, but also results in the formation of polypeptides from the amino acid molecules produced in the hydrolysis. The authors of this paper did not, however, succeed in determining the mean molecular weight of the solid compound, owing to its extremely low solubility.

The question of the effect of pressure on the rate of formation of polypeptides from amino acids and their esters is undoubtedly of great theoretical and practical interest. In view of this fact we have, in the present work, undertaken a study of the behavior of esters of amino acids under pressure. The reason for the choice of esters of amino acids as monomers is that the resulting alkoxyl end groups permit the number of units in the polymer chain formed to be determined comparatively readily, even when the polymer is insoluble in the usual organic solvents.

The simplest of the amino acid esters, the methyl ester of glycine, was selected for investigation. As early as 1888 Curtius [2], who was the first to obtain the methyl ester of glycine in the free state, found that, when this ester was left for a few days in a sealed tube, it was converted into a white solid mass. This phenomenon was given the name "polymerization", but its essential character was not discovered by Curtius. Later, in 1904 [3], the same worker showed that in the polymerization of the ethyl ester of glycine under like conditions a tetraglycyl compound was formed, namely $NH_2CH_2CO(NHCH_2CO)_3NHCH_2CO_2C_2H_5$, which was called a "biuret base" by the author. Curtius showed that, apart from the tetraglycyl compound, glycine anhydride was always present in the polymerization products. The next work on the polymerization of glycine esters appeared in 1939.

In a short communication Frankel and Katchalski [4] gave their experimental results on the polycondensation of the ethyl ester of glycine. The authors, who did not draw any theoretical conclusions, showed that by variation of the medium and temperature conditions, and by passage of gas through the ester, linear polymers of 12 to 20 units could be obtained. All of the polymers obtained were hornlike in nature and were practically insoluble in hot water. The question of the polycondensation of glycine esters is treated in greater detail in a paper by the same authors, which appeared in 1942 [5]. The data supplied by this paper concerning the polycondensation of the methyl, ethyl, and isobutyl esters of glycine are mutally complementary. The authors showed that the methyl ester of glycine, when left in an open vessel for one month, yields a fraction that is insoluble in hot water and contains 18 amino acid residues. Also, when nitrogen is passed for 12 hours and the reaction mixture is set aside for one month at room temperature, a polymer of 30 units is obtained. When the methyl ester of glycine is kept in dry ether for three months at room temperature, a polymer of 27 units can be obtained, and when the ester is boiled in dry toluene for four hours and the reaction mixture is then left for three months, a polymer containing 35 monomer units is obtained.

Frankel and Katchalski consider that the glycine ester polymers that they isolated have a straight chain structure, this contention being proved, in their opinion, by the following facts, which they have established: 1) the proved presence of alkoxyl and amino end groups; 2) the obtaining of the biuret reaction during the alkaline hydrolysis of polymer molecules; 3) the quantitative agreement between the number of glycine residues in the condensation product (calculated from the content of alkoxyl groups) and the number of amino acid molecules liberated in the complete acid hydrolysis of the condensed molecules.

The paper of Fraenkel-Conrat et. al. [6], which appeared in 1945 and was concerned with questions relating to the preparation of polyglycine esters, contains no data that are essentially different from those that we have cited. The authors kept the methyl ester of glycine in ether solution at room temperature for one month, and obtained, in addition to low polymers, highly polymeric glycine esters containing 15 glycine units. In confirmation of this value

of the chain length, the authors give analytical figures for free amino nitrogen, amino nitrogen liberated by acid hydrolysis, and bound nitrogen.

It was considered to be of interest to study the polycondensation of the methyl glycine ester under super-high pressures at various temperatures. Also, it was considered to be important to establish the structure of the polymers with certainty, for the proof given by Katchalski of the linear-chain structure is not convincing: all of the arguments given above will apply also if there are cyclic groupings in the molecule, for example 2,5-piperazinedione units.

It must be noted that according to the 2,5-piperazinedione theory, which was advanced by Zelinsky in 1914 and developed by him, in conjunction with Sadikov in 1923 [7], the protein molecule, which is a polymer formed from amino acids, is bound to contain not only polypeptide chains, but also 2,5-piperazinedione rings. The researches of Zelinsky, Gavrilov, and coworkers have shown the readiness with which 2,5-piperazinediones are destroyed, and also the possibility of the formation of 2,5-piperazinedione rings under the conditions employed for the hydrolysis of proteins with the object of determining their structure.

Gavrilov and Koperina [8] have proposed a method of electrolytic reduction which, unlike previous methods for the determination of piperazinediones, permits the presence and number of piperazinedione rings in the protein molecule to be established with exactness. We have taken this method as our basis in proving the structure of polymers of glycine methyl ester formed under conditions of normal and super-high pressures.

In the present investigation we have studied the polycondensation of glycine methyl ether at 4500 atm and at various temperatures (room, 50, 75, and 130°). At the same time, comparative experiments were carried out at atmospheric pressure. As a result of the reaction a mixture of polycondensation products was obtained, from which we separated only the macromolecular polymers, insoluble in hot water. Investigation of the reaction products showed that high pressure results in increased rate of reaction and in the degree of polycondensation. In order to decide the question of the structure of the polymers obtained, we subjected them to electrolytic reduction by Gavrilov and Koperina's method.

Our tests showed that our polymers would not undergo the electrolytic reduction reaction that was to be expected if piperazinedione rings were present in the polymer molecule. This gave us reason to suppose that linear-chain molecules may be formed when polycondensation occurs under high-pressure conditions. Calculations of the theoretical contents of amino nitrogen and methoxyl groups based on a linear-chain structure for the polycondensation products were in good agreement with the experimental results. Since the polymers obtained were insoluble in all of the organic solvents that we tried, we could determine the molecular weight (and so the number of monomer units in the polymer) only by the chemical method: by the content of methoxyl end groups. We determined the methoxyl content by Viebŏck's method, and the analytical results were confirmed by hydrolysis followed by determination of amino nitrogen by titration according to the methods of Sorensen and Linderström-Lang, and also by the preparation of copper salts.

EXPERIMENTAL

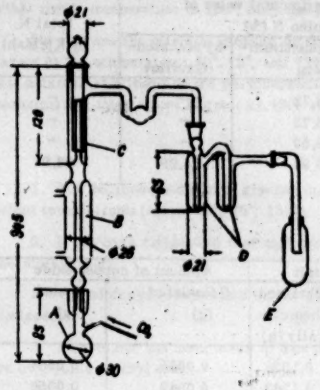
Preparation of Starting Materials. The methyl ester of glycine was prepared by the method proposed by Frankel and Katchalski in which the hydrochloride of glycine methyl ester is suspended in absolute ether and decomposed by a current of dry ammonia at 0°; it had the following constants: b.p. 46.5° (12 mm); 48.5° (16 mm); 54° (20 mm). For glycine methyl ester the literature gives: b.p. 45° (20 mm) [5]; b.p. 130° (760 mm) [6]; 54° (50 mm), average yield 48.4% [2]. In its turn the hydrochloride of glycine methyl ester was prepared by the following series of reactions: glycine $\xrightarrow{HCl}$ glycine hydrochloride $\xrightarrow{HCl,\ CH_3OH}$ hydrochloride of glycine methyl ester, m.p. 174.5-175° (the literature [2] gives 175°).

Found %:	C 28.73; 28.94;	H 6.62; 6.59;	N 11.44; 11.32
$C_3H_8O_2NCl$. Calculated %:	C 28.69	H 6.42	N 11.16

Experimental Procedure. The experiments on polycondensation under pressure were carried out in a strong tube of plastic material, length 10 cm, internal diameter 6.5 mm, wall thickness 2.5 mm. The ends of the tube were provided with pistons, by means of which the pressure was communicated to the substance under investigation; the tube was encased in copper. It was placed in a high-pressure reactor filled with freshly distilled, anhydrous glycerol. The reactor was immersed in an oil bath provided with electric heater, stirrer, and contact and control thermometers. The pressure was applied by means of a hydraulic compressor. The variation from the stipulated experimental temperatures did not exceed $\pm 1°$.

The routine was the same for all of the pressure experiments; it was as follows: For the first 18 hours the glycine methyl ester was under pressure at room temperature. Heat was then applied for six hours (pressure experiments

were carried out at elevated temperature), and 18 hours after heating ceased the pressure was released. Hence, the glycine methyl ester was under pressure for 42 hours altogether, and this period included six hours during which heat was applied.



Apparatus for the quantitative determination of methoxyl content: A) reaction vessel; B) condenser; C) column containing a suspension of red phosphorus in water; D) absorption vessel containing a mixture of sodium acetate, acetic acid, and bromine; E) absorption vessel containing a mixture of sodium acetate and formic acid.

The polycondensation reaction carried out at the same temperatures, but under atmospheric pressure, was performed in glass tubes protected by soda-lime tubes and immersed in an oil thermostat. As in the pressure experiments, the reaction proceeded for 18 hours at room temperature, heating was then applied for six hours, and after a further 18 hours at room temperature the experiment was concluded. The routine in the experiments at high pressure and at atmospheric pressure was therefore the same.

Treatment of the Reaction Products

The product obtained as a result of the polymerization was transferred to a weighed tube for centrifugation, and was washed in the centrifuge with hot water until the washings showed a negative reaction with picric acid (absence of 2,5-piperazinedione) and a negative biuret reaction (absence of low polymers, soluble in water). The water-insoluble polymerization product was dried in a vacuum desiccator. When constant weight was attained, the electrolytic reduction of the product was carried out, the methoxyl content was determined, and the product was hydrolyzed with 25% hydrochloric acid and then determined as the copper salt of glycine.

Determination of Cyclic Groupings in the Polymers by the Electrolytic-reduction Method. The electrolytic reduction of the product was carried out by the method of Gavrilov and Koperine [8]. In the hydrolyzates obtained before and after reduction, the total nitrogen was determined by the Kjeldahl method and the amine nitrogen by Sörensen's method, as modified by Gavrilov. The results of the electrolytic reduction of the product obtained by the polycondensation of glycine methyl ester at 4500 atm and 75° are presented in Table 1.

TABLE 1
Analysis for Nitrogen in Different Forms, Before and After Reduction

Conditions of experiment	Total N in solution (g)	Amino N	
		(g)	(% of total N)
Before reduction after hydrolysis	0.0474	0.0485	102.32
After reduction after hydrolysis	0.0376	0.0380	101.06

As will be seen from Table 1, no reduction in the amount of nitrogen titratable by Sörensen's method in the hydrolyzate of the product obtained after electrolytic reduction is observed, which may be taken as a proof of the absence of 2,5-piperazinedione rings.

TABLE 2
Quantitative Determination of the Methoxyl Content by Viebock's Method

Conditions under which product obtained		CH_3O content (%)
Pressure (atm)	Temperature (°C)	
1	75°	2.16
4500	50	0.71
4500	75	0.80
4500	130	0.95

We determined the methoxyl content by Viebock's method [9].

In the course of the work we introduced some slight modifications in the apparatus (see figure). Also, instead of the recommended hydriodic acid of sp.gr. 1.7, we used acid of sp.gr. 1.96. The analytical results are given in Table 2.

The hydrolysis of the product for amino nitrogen determination was carried out with 25% hydrochloric acid at the boil for six hours. The hydrolyzate was

TABLE 3

Quantitative Determination of Amino Nitrogen by Titration by the Methods of Linderström-Lang and Sörensen, and of Total Nitrogen by the Kjeldahl Method

Substance	Amino N calculated theoretically from methoxyl content (%)	Experimental value of amino N (%)		Total N by Kjeldahl
		by Linderström-Lang	by Sörensen-Gavrilov	
Glycine	18.66	18.72	–	–
Glycine	18.66	18.75	–	–
Glycine	18.66	18.50	–	–
Product obtained at 75° and 4500 atm	24.35	23.90	24.29	23.91

TABLE 4

Quantitative Determination of the Copper Salt

Conditions under which product obtained		Amount of copper salt		Amount of copper oxide	
Pressure (atm)	Temperature (°C)	Calculated theoretically from methoxyl content (g)	Obtained theoretically (g)	Calculated (g)	Found (g)
4500	75	0.1377	0.1338	0.0065	0.0064
4500	75	0.1373	0.1363	0.0049	0.0050

TABLE 5

Effect of Pressure and Temperature on the Rate of the Polycondensation of Glycine Methyl Ester and on the Mean Molecular Weight of the Product

Pressure (atm)	Temperature (°C)	Methoxyl content (%)	Mean no. of groups	Mean molecular weight	Yield (%)
1	Room	No Product Obtained			
1	50	Traces of Product			
1	75	2.16	25	1458	4.08
4500	Room	No Product Obtained			
4500	50	0.71	76	4368	10.61
4500	75	0.80	67	3855	13.04
4500	130	0.95	57	3284	18.91

neutralized with caustic soda solution, and the amino nitrogen was determined by titration, following Sörensen and Linderström-Lang [10]. This procedure was first checked with glycine. The product obtained at 75° and 4500 atm was analyzed in this way (Table 3).

The quantitative determination of the copper salt was carried out by Heintz's method [11], and for this purpose the product was hydrolyzed with 10% sulfuric acid at the boil (Table 4).

As will be seen from the tables, the results for the amino-nitrogen and copper salt estimations were is good agreement with the methoxyl-determination results.

Discussion of Results. In Table 5 we give data showing the dependence of the rate of polycondensation of glycine methyl ester and the mean molecular weight of the product on pressure and temperature.

It will be seen from Table 5 that at 50° and atmospheric pressure only traces of macromolecular polypeptides are obtained, and it was not found possible to analyze these owing to the small amount formed. At 4500 atm, however, at the same temperature, a mixture of macromolecular polypeptides was obtained in 10% yield, and the methoxyl content, 0.7%, corresponded to an average of 76 monomer units per molecule, if we assume the polypeptides formed to be of linear structure. In the experiments at 75° and atmospheric pressure, a mixture of water-insoluble polypeptides was obtained in 4.08% yield, and the methoxyl content, 2.16%, corresponded to a mean chain length of 25 monomer units. At 4500 atm and at the same temperature, the yield of macromolecular polypeptides was 13%, and the methoxyl content was 0.80%, corresponding to an average of 67 monomer units per molecule.

These experiments show also the effect of temperature on the course of the polycondensation of the glycine ester under pressure. As Table 5 shows, no macromolecular reaction products are formed at room temperature. At 50° and 75° the effect of rise of temperature on the reaction rate and degree of polymerization is seen, but with further rise in temperature to 130°, only the yield of macromolecular polypeptides increases.

We thus see the effect of pressure on the rate of polycondensation and on the mean molecular weight of the product at the temperatures 50°, 75°, and 130°. At 75°, for example, both the yield of macromolecular polypeptides obtained as a result of the polycondensation reaction and the mean molecular weight of these products are approximately three times as great at 4500 atm as at atmospheric pressure.

SUMMARY

1. The polycondensation of glycine methyl ester has been investigated at a pressure of 4500 atm and at various temperatures (room, 50°, 75°, 130°).

2. It has been established that high pressure increases the rate and extent of the polycondensation of glycine methyl ester.

3. The effect of temperature on the polycondensation of glycine methyl ester under pressure has been determined.

4. An attempt has been made to determine the structure of the products of the polycondensation under pressure of glycine methyl ester.

Received January 15, 1953.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 11. BEHAVIOR OF 2-METHYL-2-BUTENE AND 2,3-DIMETHYL-2-BUTENE IN THE CATALYTIC HYDROCONDENSATION REACTION

Ya. T. Eidus, K. V. Puzitsky, and A. P. Meshcheryakov

The catalytic hydrocondensation of carbon monoxide with olefins has been now effected with ethylene and its closest homologs, the α-olefins [1]. Experiments with the object of extending the reaction to 2-methylpropene [2] showed that this unsymmetrical dimethylethylene readily enters into hydrocondensation with carbon monoxide, and that the active part of the molecule is the unsubstituted methylene group. This is evident from the fact that the reaction products consist essentially of hydrocarbons having a methyl side group on the second carbon atom.

The present investigation had the object of studying the behavior of tri- and tetra-substituted ethylenes, i.e., 2-methyl-2-butene and 2,3-dimethyl-2-butene, in the reaction of hydrocondensation with carbon monoxide. It is of interest to note that according to the literature [3] these two hydrocarbons do not enter directly into the catalytic oxo-synthesis reaction, i.e., into the reaction leading to the synthesis of alcohols from olefins, carbon monoxide, and hydrogen under pressure. Under the conditions of this synthesis 2-methyl- and 2,3-dimethyl-2-butenes are first isomerized to α-olefins, which then enter into the oxo-synthesis reaction with formation of the corresponding alcohols.

EXPERIMENTAL

Synthesis of 2-Methyl-2-butene and 2,3-Dimethyl-2-Butene

For the synthesis of 2-methyl-2-butene, we used fermentation amyl alcohol, which was dehydrated over aluminum oxide at 450-500° to a mixture of 3-methyl-1-butene, 2-methyl-1-butene, and 2-methyl-2-butene. This mixture of pentene isomers was treated, following Vyshnegradsky [4, 5] with dilute sulfuric acid under ice cooling. The 3-methyl-1-butene, which remained in the upper layer, was separated, and the lower layer was diluted with water and hydrolyzed. The product was distilled twice, and the fraction of b.p. 37-38° was again distilled over sodium, yielding 85 ml of a fraction (2-methyl-2-butene), b.p. 37-38° at 753 mm. The 2-methyl-2-butene obtained comprised about 45% of the original mixture of pentene isomers, and it had the following constants: b.p. 37-38° (753 mm); d_4^{20} 0.6590; n_D^{20} 1.3860; Found MR 24.98; Calculated MR 24.82. The literature [6, 7] gives: b.p. 38.5-38.6° (760 mm); d_4^{20} 0.6620; 0.6596; n_D^{20} 1.3869; 1.3876.

We prepared 2,3-dimethyl-2-butene according to the scheme:

$$(CH_3)_3CCOCH_3 \xrightarrow{H_2} (CH_3)_2CCH(OH)CH_3 \xrightarrow{Al_2(SO_4)_3} (CH_3)_2C=C(CH_3)_2 + H_2O.$$

Pinacolyl alcohol was prepared by hydrogenation of pinacolone (b.p. 106°) in presence of a 30% Bag nickel catalyst [8], the initial hydrogen pressure being 80-100 atm and the temperature 160-180°. The pinacolyl alcohol obtained (220 ml) was fractionated, and the fraction of b.p. 118-120° at 757 mm (90%) was then dehydrated over anhydrous aluminum sulfate prepared by the method indicated above.

According to the literature [9], pinacolyl alcohol, and also the normal product of its dehydration, 3,3-dimethyl-1-butene, are converted in the vapor phase in presence of anhydrous aluminum sulfate at 275° into a mixture of products containing 62-63% of 2,3-dimethyl-2-butene, 33-34% of 2,3-dimethyl-1-butene, and 3.5-4.3% of 3,3-dimethyl-1-butene.

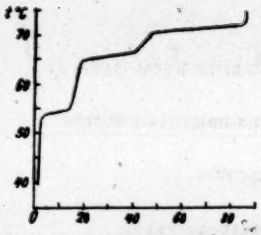

Fig. 1. Fractionation curve for the product of the dehydration of pinacolyl alcohol over aluminum sulfate.

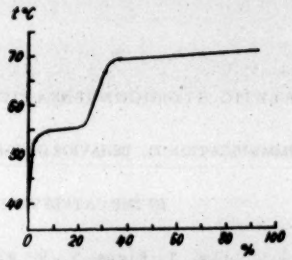

Fig. 2. Fractionation curve for the product of the dehydration of Fractions I-V (Table 1) over aluminum sulfate.

TABLE 1

Fraction No.	Boiling range (°C)	Amount (% by volume of original catalyzate)	d_4^{20}	n_D^{20}
I	40-54.5	5.2	0.6712	1.3881
II	54.5-57	9.6	0.6922	1.3920
III	57-66	5.9	0.6904	1.4038
IV	66-67	21.6	0.6933	1.4027
V	67-71	5.9	0.6987	1.4070
VI	71-73	37.7	0.7075	1.4128
Residue	–	7.4	–	–
Losses	–	6.7	–	–

From 200 ml of pinacolyl alcohol dehydrated for 27 hours at 275° over anhydrous aluminum sulfate, 170 ml of catalyzate and 20 ml of water were obtained. The catalyzate was separated from the water, washed, dried, and fractionated through a 40-plate column having a filling of single metal spirals. The volume of catalyzate taken for fractionation was 135 ml; the fractionation curve, obtained for a pressure of 744 mm, is given in Table 1.

Fraction VI (53 ml, b.p. 71-73°) had the constants d_4^{20} 0.7075 and n_D^{20} 1.4128, and consisted of 2,3-dimethyl-2-butene: Found MR 29.62; Calculated MR 29.44. For 2,3-dimethyl-2-butene the literature [6] gives: b.p. 73.2° at 760 mm; d_4^{20} 0.7088; n_D^{20} 1.4121.

Fractions I-V were united, and 54 ml was again passed at 275° for five hours over a fresh portion (75 ml) of anhydrous aluminum sulfate, yielding 51 ml of catalyzate, which was washed, dried, and fractionated (740 mm) as before. The curve for the fractionation of 43 ml is given in Fig. 2.

Two fractions were taken: Fraction I (17 ml), boiling range 41-70°, and Fraction II (22 ml), boiling range 70-71.6°, d_4^{20} 0.7086; n_D^{20} 1.4120. Fraction II, which consisted of 2,3-dimethyl-2-butene (Found MR 24.53; Calculated 24.44), was united with the corresponding fraction of the first catalyzate. In this way 75 ml of 2,3-dimethyl-2-butene was obtained and was used in the experiments on hydrocondensation with carbon monoxide. It may be noted that the low plateaus on the fractionation curves in Fig. 1 and 2 (b.p. 55-56°) correspond to 2,3-dimethyl-1-butene (the literature [6] gives b.p. 55.6°).

Experiments on the Hydrocondensation of Carbon Monoxide with 2-Methyl-2-butene and 2,3-Dimethyl-2-butene

The apparatus and procedure were the same as in the previous work on 2-methylpropene [2]. The experiments were carried out at 190° and atmospheric pressure in a continuous-flow system. The activity of the catalyst was checked beforehand in the hydrocondensation reaction of carbon monoxide with ethylene, and it was found to be high (yield of condensate 500 ml per cu. m at a space velocity of 100 liter/liter·hr.).

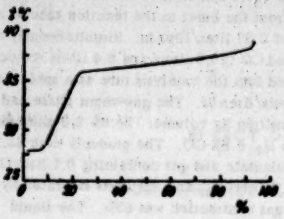

Fig. 3. Fractionation curve for the product of the hydrocondensation of carbon monoxide with 2-methyl-2-butene.

Experiments with 2-Methyl-2-butene. 2-Methyl-2-butene (85 ml, i.e., 0.8 mole) was passed from the buret to the reaction tube, which contained a 40-cm layer of Catalyst No. 52; a space velocity of 0.31 liter/liter·hr was maintained for nine hours. Simultaneously, a mixture of hydrogen and carbon monoxide was passed into the catalysis tube at a space velocity of 70 liters/liter·hr, the total amounts passing being 2.6 liters of CO and 24.5 liters of H_2. The gas-vapor phase had the following composition by volume: 39.7% 2-methyl-2-butene, 54.4% H_2, 5.9% CO. The liquid catalyzate obtained (75.0 ml) was dried with anhydrous copper sulfate and 51 ml of it was fractionated at 750 mm through the column described above. The fractionation curve is given in Fig. 3.

It will be seen from Fig. 3 that 93% by volume of the catalyzate distilled within the range 28-37.5°. The residue was distilled from a Favorsky flask over the range 55-240°. The fractions taken and their properties are given in Table 2.

It will be seen from Fig. 3 and Table 2 that 94% of the catalyzate consisted of C_5 hydrocarbons.

It would be expected that hydrogenation of 2-methyl-2-butene would yield 2-methylbutane (b.p. 27.9°, d_4^{20} 0.61972; n_D^{20} 1.3539 [6]). It can be seen from the properties of the condensate fractions obtained that Fractions I and II, comprising about 33% by volume, consist of 2-methylbutane contaminated with unchanged 2-methyl-2-butene, and Fractions III-IV, which comprise 60%, are essentially 2-methyl-2-butene. Fraction V can be considered as consisting of the products of hydrocondensation with carbon monoxide and the products of hydropolymerization, but it comprises only 5.9% by volume of the catalyzate. This fraction is mainly produced by the transformation of the original 2-methyl-2-butene, since not more than 0.5 ml of condensate can be obtained by synthesis from CO and H_2.

TABLE 2

Fraction No.	Boiling range (°C)	Amount (% by volume of original catalyzate)	d_4^{20}	n_D^{20}
I	28-29	11.8	0.6260	1.3635
II	29-36	21.5	0.6342	1.3780
III	36-37	23.5	0.6535	1.3832
IV	37.0-37.5	36.3	0.6585	1.3860
V	55-240	5.9	0.6729	1.3930

TABLE 3

Fraction No.	Boiling range (°C)	Amount (% by volume of original catalyzate)	d_4^{20}	n_D^{20}
I	28-30	3.8	—	1.3513
II	48-58	7.7	0.6555	1.3745
III	58	17.3	0.6626	1.3766
IV	58.5-63	19.2	0.6652	1.3794
V	63-71	18.5	0.6754	1.3988
VI	71-73	24.0	0.7096	1.4111
VII	80-137	11.5	0.7047	1.3989
Residue and losses	Above 137	3.0	—	—

It may therefore be regarded as established that, under the given conditions, only 5-6% of the 2-methyl-2-butene entered into the reaction of hydrocondensation with carbon monoxide, and 30-35% was hydrogenated to 2-methylbutane.

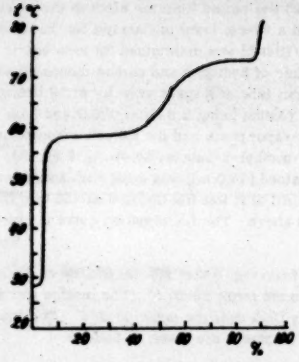

Fig. 4. Fractionation curve for the product of the hydrocondensation of carbon monoxide with 2,3-dimethyl-2-butene.

Experiments with 2,3-Dimethyl-2-butene. 2,3-Dimethyl-2-butene (63.5 ml, i.e., 0.53 mole) was passed for eight hours from the buret to the reaction tube at a space velocity of 0.37 liter/liter·hr. Simultaneously a mixture of H_2 and CO (20.9 liters and 2.4 liters respectively) was passed into the catalysis tube at a space velocity of 116 liters/liter·hr. The gas-vapor phase had the following composition by volume: 34.0% 2,3-dimethyl-2-butene, 59.2% H_2, 6.8% CO. The products were 63.7 ml of liquid condensate and gas containing 0.1 liter CO, 0.2 liter CO_2, 5.0 liters H_2, and 3.2 liters saturated hydrocarbons; the gas contraction was 65%. The liquid catalyzate was dried over anhydrous copper sulfate, and 52 ml of it was fractionated at 745 mm through the same column. The fractionation curve (Fig. 4) shows that 92% by volume of the catalyzate distilled within the range 28-81°. The residue boiling above 81° comprised 7% of the total; it was distilled from a Favorsky flask over the range 84-137°, and the further residue that then remained amounted to 1%.

The fractions taken and their properties are given in Table 3. Fractions obtained in amounts of less than 0.3% are not given in Table 3.

It will be seen from Fig. 4 and Table 3 that the catalyzate consisted mainly of unchanged 2,3-dimethyl-2-butene and its hydrogenation product, 2,3-dimethylbutane. Fractions III and IV and most of Fraction II were 2,3-dimethylbutane (b.p. 58°, d_4^{20} 0.6616; n_D^{20} 1.3750 [6]). Fraction VI and much of Fraction V consisted of unchanged 2,3-dimethyl-2-butene. Fraction I and part of Fraction II contained C_5 hydrocarbons. Fraction VII may be considered to have resulted from hydrocondensation. This fraction, which comprised 11.5% by volume, was obtained from 2,3-dimethyl-2-butene, for calculation shows that not more than 1 ml of catalyzate could be obtained by synthesis from CO and H_2. These results show that 2,3-dimethyl-2-butene enters into hydrocondensation with carbon monoxide to the extent of only 10%; hydrogenation with formation of 2,3-dimethylbutane occurs to the extent of about 50%.

SUMMARY

1. The behavior of 2-methyl-2-butene and 2,3-dimethyl-2-butene in the reaction of hydrocondensation with carbon monoxide has been investigated.

2. It has been found that 2-methyl-2-butene enters into the hydrocondensation reaction to an extent of only 5-6%, and undergoes hydrogenation to 2-methylbutane to the extent of 30-35%.

3. Under the conditions of the hydrocondensation reaction, 2,3-dimethyl-2-butene is hydrogenated to 2,3-dimethylbutane to the extent of about 50%. About 10% of it undergoes the hydrocondensation reaction.

Received January 17, 1953.

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EFFECT OF COMPRESSION ON THE PROPERTIES OF DEHYDROGENATION AND DEHYDRATION CATALYSTS

L. F. Vereshchagin, L. Kh. Freidlin, I. U. Numanov and S. G. Kulikov

Only a few data are available in the literature concerning the behavior of catalysts that have been subjected to compression under high pressures [1], and the few catalysts that have been examined were of a mixed type. In this, as in the previous investigations [2, 3], a study has been made of the effect of compression on simple, one-component catalysts, namely, zinc, titanium, and thorium oxides, and normal calcium phosphate in the dehydrogenation and dehydration reactions that are characteristic for these catalysts.

EXPERIMENTAL

Experimental Conditions

The catalyst was placed in a tube of pure aluminum, length 50 mm, diameter 10 mm. The tube was closed, placed in the channel of the multiplier, and subjected to a pressure of 20,000 atm. The compression procedure has been described in detail in a previous communication [2].

The compressed tube was cut along its length, and the catalyst was taken out. The reaction was performed by the continuous-flow method with 10 ml of catalyst. The experimental conditions and results are given in the tables.

Dehydrogenation of Isobutyl Alcohol over Zinc Oxide

The data in the literature on the catalytic selectivity of zinc oxide are contradictory. Zinc oxide is generally regarded as a dehydrogenation catalyst, but Adkins [4] has succeeded in preparing samples of zinc oxide having dehydration properties. He explained this great change in the selectivity of this oxide catalyst by peculiarities in the conditions of its preparation and treatment. Agronomov [5] has studied this subject and has concluded that the varying activity of zinc oxide samples in the dehydrogenation of isobutyl alcohol are due not to differences in the parameters of the crystal lattice, but to variations in specific surface.

Kutseva [6] found that zinc oxide, free from any promoter, selectively catalyzed the dehydrogenation of isobutyl alcohol. Variation in the method of preparation of the zinc oxide and its treatment with ultraviolet radiation or X-rays had no effect on its selectivity; only the addition of foreign substances affected its specificity. According to these results, it was to be expected that compression also would not affect the selectivity of the action of zinc oxide.

TABLE 1

Dehydrogenation of Isobutyl Alcohol over Noncompressed and Compressed Zinc Oxide

Catalyst	Temperature of experiment (°C)	Volume of gas evolved per 1 ml of alcohol (ml)	Composition of gas* (%)			Degree of conversion of alcohol (%)
			CO_2	CO	H_2	
Noncompressed 10 ml, 5.6 g	340	50.4	1.2	0.2	98.6	20.6
	360	114.1	1.2	0.3	98.5	47.2
	380	196.3	1.2	0.4	98.4	79.5
Compressed 10 ml, 18.5 g	340	83.6	1.2	0.2	98.6	33.8
	360	166.1	1.2	0.2	98.6	67.7
	380	240.2	1.4	0.9	97.7	97.1

*No saturated or unsaturated hydrocarbons were detected in the gas.

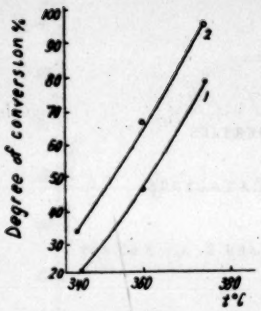

Fig. 1. Dehydrogenation of isobutyl alcohol over ZnO: 1) noncompressed; 2) compressed.

The zinc oxide was prepared by precipitation of a molar solution of zinc nitrate with a normal solution of sodium carbonate. The precipitate was washed, molded, and heated for 10-12 hours at 350°. The specific surface of zinc oxide prepared in this manner should be about 50 sq.m/g. In all experiments the space velocity was 0.28 liter/liter·hr.

It will be seen from Table 1 that both compressed and noncompressed zinc oxide selectively catalyze the decomposition of isobutyl alcohol in the direction of dehydrogenation. At 340° the degree of conversion of isobutyl alcohol over compressed catalyst is approximately 70% higher than over noncompressed catalyst, and the corresponding figures for 360° and 380° are 45% and 24% respectively.

Both of the samples of zinc oxide were submitted to X-ray analysis (chromium K series λ = 2.285 A). The following results were obtained:

Sample before compression	a = 3.15 A and c = 5.08 A
Sample after compression	a = 3.19 A and c = 5.11 A
Data from t ables	a = 3.24 A and c = 5.18 A

After compression, therefore, the parameters of the zinc oxide lattice had changed only slightly.

Kinetics of the Decomposition of Ethyl Alcohol over Titanium Dioxide

As Rubinshtein and Kulikov [7] have shown, titanium dioxide in the form of anatase preferentially catalyzes dehydration, whereas the rutile form favors dehydrogenation; also, the pure forms taken separately are less active than a mixture of the two. Under the temperature conditions necessary for the decomposition of alcohol, both modifications of titanium oxide are generally present.

On account of the tendency of titanium dioxide to undergo polymorphic changes, it was of interest to find out whether any such change could take place during compression, and so affect its catalytic activity and specificity in the decomposition of ethyl alcohol. The titanium oxide was prepared from titanium tetrachloride by precipitation with dilute aqueous ammonia.

The results obtained are given in Table 2 and Fig. 2-5.

TABLE 2

Decomposition of Ethyl Alcohol over Compressed and Noncompressed Titanium Dioxide.

Catalyst	Temperature of experiment (°C)	Volume of gas evolved per 1 ml of alcohol (ml)			Degree of conversion (%)			Heat of dehydrogenation (cal/mole)
		H_2	C_2H_4	C_2H_6	Dehydrogenation	Dehydration	Total	
Noncompressed: Vol. 10 ml, Wt. 8.8 g	360	14.3	82.5	60.6	19.5	37.0	56.5	
	380	18.6	105.7	68.8	22.7	45.5	68.2	7200
	400	28.0	110.2	76.8	27.3	48.7	76.0	
Compressed: Vol. 10 ml, Wt. 17.5 g	360	13.0	115.1	46.0	15.0	42.3	57.3	
	380	17.4	118.3	48.2	16.8	43.0	59.8	7200
	400	21.8	106.9	58.6	21.0	43.0	64.0	

It will be seen from Table 2 that, apart from the products of the two main reactions (ethylene and hydrogen) ethane is formed also. Hence, in the calculation of the degree of conversion of alcohol in the two directions, the volume of ethane formed is recalculated as ethylene and hydrogen, and the values obtained are added to the analytically found volumes of ethylene and hydrogen.

It will be seen from Table 2 and Fig. 2 that the total degree of conversion of ethyl alcohol at 360° is the same over compressed catalyst as over noncompressed catalyst. With rise in temperature the degree of conversion in presence of noncompressed catalyst rises from 56.5% at 360° to 76% at 400°. In presence of compressed catalyst, however,

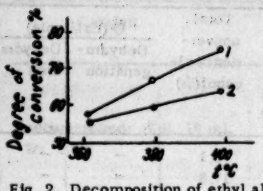

Fig. 2. Decomposition of ethyl alcohol over TiO_2: 1) noncompressed; 2) compressed.

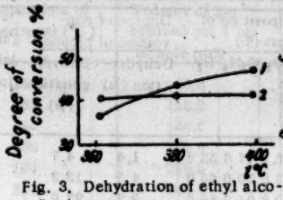

Fig. 3. Dehydration of ethyl alcohol over TiO_2: 1) noncompressed; 2) compressed.

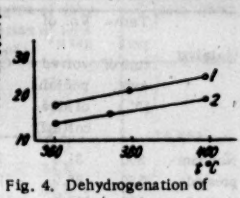

Fig. 4. Dehydrogenation of ethyl alcohol over TiO_2: 1) noncompressed; 2) compressed.

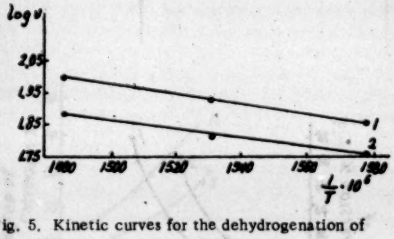

Fig. 5. Kinetic curves for the dehydrogenation of ethyl alcohol over TiO_2: 1) noncompressed; 2) compressed.

there is a smaller increase in the degree of conversion under these conditions: from 57.3% at 360° to 64% at 400°.

Let us examine the way in which the rates of the three different reactions vary. Over noncompressed catalyst the rate of the dehydration of alcohol rises sharply with rise in temperature, whereas over compressed catalyst it remains constant. Also, the reaction rate over the compressed sample is appreciably higher at 360°, somewhat lower at 380°, and considerably lower at 400° than the rate of the noncompressed catalyst (Fig. 3). On the other hand, dehydrogenation and hydrogenation reactions (Fig. 4) proceed at an appreciably higher rate over the noncompressed sample than over the compressed sample.

The results show that compression of the catalyst has less effect on its activity for the dehydration of alcohol than on its activity for the dehydrogenation of alcohol or hydrogenation of ethylene. The activation energy for the dehydrogenation reaction is the same for both titanium dioxide samples, and has a value of 7200 cal/mole (Fig. 5). It would appear that the reduction in rate of dehydrogenation over a compressed sample (in comparison with the rate of dehydration over the sample) is associated not with change in the nature of the active centers, but with increase in the difficulty with which the products of this reaction (mainly acetaldehyde) undergo desorption from the surface of the catalyst after it has been compressed so that the volume of the conveying pores has probably been reduced.

Kinetics of the Decomposition of Ethyl Alcohol over Thorium Dioxide

It is known that thorium dioxide is able to catalyze the decomposition of alcohols in two directions simultaneously: dehydrogenation and dehydration. The method by which it is prepared is of considerable importance. In Tolstopyatova's experiments [8] thorium dioxide prepared by precipitation of thorium nitrate with ammonia was found to catalyze the decomposition of ethyl alcohol at 300° so that mainly (85-90%) dehydrogenation occurred. When the temperature was raised to 420°, the degree of dehydrogenation fell to 40-50%, and the degree of dehydration rose from 10-12% to 40%.

We have now studied the comparative activity of compressed and noncompressed thorium dioxide prepared by precipitation of thorium nitrate with ammonia. The catalyst was washed, dried at 110-120°, and then dehydrated for 9-10 hours at 340-350°. Alcohol was passed at a space velocity of 0.75 liter/liter · hr. The results obtained are given in Table 3 and Fig. 6-9.

It will be seen from Table 3 that both compressed and non-compressed thorium dioxide samples catalyze both decomposition processes, and also the side process of carbon monoxide and carbon dioxide formation. The amount of carbon oxides in the gaseous reaction products varied from 19 to 22% for the noncompressed catalyst and from 15 to 17% for the compressed catalyst. Since this side process of carbon oxide formation occurs at almost identical rates on the two catalysts at various temperatures, the kinetics of the two main processes of alcohol decomposition may be examined independently of the rate of the side reaction. The activity of compressed thorium dioxide (per unit

TABLE 3

Decomposition of Ethyl Alcohol in Presence of Noncompressed and Compressed Thorium Dioxide

Catalyst	Temperature of expt. (°C)	Vol. of gas evolved per 1 ml of alcohol (ml)	Composition of gas (%)				Degree of conversion of alcohol		Dehydrogenation/dehydration ratio	Total conversion of alcohol (%)	Q (cal/mole)	
			CO	CO_2	C_2H_4	H_2	Dehydration (%)	Dehydrogenation (%)			Dehydrogenation	Dehydration
Noncompressed: Vol. 10 ml, Wt. 8.6 g	300	31.3	7.1	16.9	17.6	58.3	1.4	4.7	3.3	6.1	–	–
	330	88.0	10.0	10.0	20.0	60.0	4.5	13.3	3.0	17.8	–	–
	350	177.6	10.0	9.8	21.2	59.0	9.7	27.0	2.8	36.7	27 500	27 500
	370	360.0	10.0	9.0	23.0	58.0	21.3	53.5	2.5	74.8	–	–
Compressed: Vol. 10 ml, Wt. 13.0 g	300	49.1	9.0	6.3	17.2	67.5	2.7	8.5	3.1	10.7	–	–
	330	160.0	10.0	6.0	21.5	62.5	8.8	25.6	2.9	34.4	30 500	30 500
	350	312.0	10.0	6.4	23.4	60.2	18.7	48.2	2.6	66.9	–	–

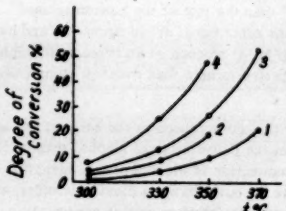

Fig. 6. Decomposition of ethyl alcohol over ThO_2: 1) dehydration over noncompressed; 2) dehydration over compressed; 3) dehydrogenation over noncompressed; 4) dehydrogenation over compressed.

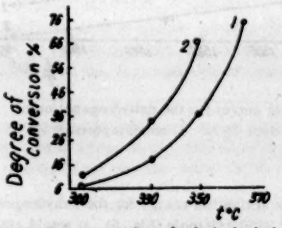

Fig. 7. Decomposition of ethyl alcohol over ThO_2: 1) noncompressed; 2) compressed.

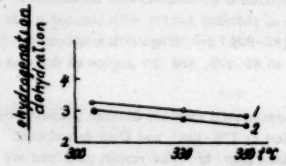

Fig. 8. Dehydrogenation/dehydration ratio for ethyl alcohol over ThO_2: 1) noncompressed; 2) compressed.

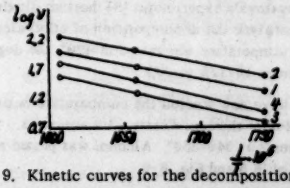

Fig. 9. Kinetic curves for the decomposition of ethyl alcohol over ThO_2: 1) dehydrogenation over noncompressed; 2) dehydrogenation over compressed; 3) dehydration over noncompressed; 4) dehydration over compressed.

TABLE 4

Kinetics of the Dehydration of Formic Acid over Noncompressed and Compressed Normal Calcium Phosphate

Catalyst	Temperature of experiment (°C)	Volume of gas evolved per 1 ml of acid (ml)	Degree of dehydration of acid (%)	Q (cal/mole)
Noncompressed: Vol. 10 ml, Wt. 5.8 g	180	90.8	15.3	14 300
	188	113.2	19.6	
	194	146.0	24.9	
	200	174.6	30.2	
	204	200.0	34.6	
	214	260.0	45.0	
Compressed: Vol. 10 ml, Wt. 12.8 g	204	122.3	21.1	14 300
	194	91.1	15.7	
	216	179.0	30.8	
	188	69.4	12.2	
	214	162.8	28.1	

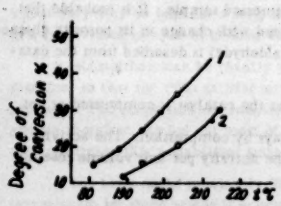

Fig. 10. Decomposition of HCOOH over $Ca_3(PO_4)_2$: 1) noncompressed; 2) compressed.

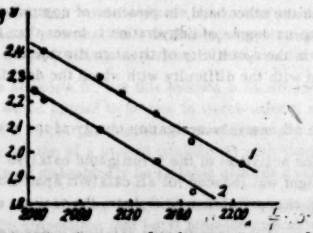

Fig. 11. Kinetic curves for the dehydration of HCOOH over $Ca_3(PO_4)_2$: 1) noncompressed; 2) compressed.

volume) is greater than that of the noncompressed catalyst in both reactions, dehydrogenation and dehydration (Fig. 6). The overall rate of decomposition of alcohol is also greater for the compressed catalyst than for the noncompressed catalyst (Fig. 7).

The ratio of the degrees of dehydrogenation and dehydration of alcohol over the range 300-350° remains almost constant for both samples of thorium dioxide (Fig. 8). This indicates that compression does not affect the selectivity in the action of the catalyst. In Fig. 9 the conformity with the Arrhenius equation is shown for the two reactions over the range 300-350°. The activation energies of the two reactions are the same on compressed and noncompressed catalyst: Q_{H_2} = 27,500 cal/mole and Q_{-H_2} = 30,000 cal/mole.

Kinetics of the Dehydration of Formic Acid over Normal Calcium Phosphate

As the work of Freidlin and Levit has shown, calcium phosphate is an extremely active catalyst of exceptionally high selectivity for the reaction of the dehydration of formic acid [9]. Already at 276° formic acid (concentration 82%) undergoes complete conversion (the carbon monoxide content of the gas obtained is 100%). The apparent activation energy of the reaction is 15,200 cal/mole.

In this work we again used a catalyst prepared from calcium chloride and ammonium phosphate; and we again used 82% formic acid. In all experiments the rate of passage of acid was 1.5 liters/liter·hr.

As will be seen from Table 4, the catalyst fully retained its high specificity when compressed: the carbon monoxide content of the gas was 100%, and there were no side processes.

The results show that after compression the activity of the catalyst is reduced by a factor of 1.5-2, when expressed in terms of unit volume, and by a factor of 3-4, when expressed in terms of unit weight (Fig. 10). The

apparent activation energy for the reaction is the same as that for the noncompressed catalyst, and has the value 14,300 cal/mole (Fig. 11). Both of the catalyst samples were investigated by X-rays (chromium K series, λ = = 2.285 A). No change in crystal structure could be detected.

SUMMARY

1. A study has been made of the effect of compression at 20,000 atm on the properties of zinc oxide, titanium dioxide, thorium dioxide, and normal calcium phosphate in dehydrogenation and dehydration reactions characteristic for these catalysts.

2. It has been shown that as a result of compression the apparent specific volume of these catalysts is reduced by the factors indicated:

Zinc oxide	3,3
Titanium dioxide	2,0
Thorium dioxide	1,5
Calcium phosphate	2,2

3. The selectivities in the action of zinc oxide in the dehydrogenation of isobutyl alcohol and in the action of calcium phosphate in the dehydration of formic acid were fully retained after compression. In the case of thorium dioxide also, compression had no effect on the relative rates of the two courses of the decomposition of ethyl alcohol. On the other hand, in presence of compressed titanium dioxide the ratio of the degree of dehydrogenation of alcohol to its degree of dehydration is lower than in presence of the noncompressed sample. It is probable that the change in the specificity of titanium dioxide due to compression is associated with change in its porosity characteristics and with the difficulty with which the dehydrogenation product (acetaldehyde) is desorbed from the catalyst.

4. In all cases the activation energy of the reaction is the same, whether the catalyst is compressed or not.

5. The activities of the investigated catalysts were altered in various ways by compression. The activity per unit weight was reduced for all catalysts apart from thorium dioxide, but the activity per unit volume rose for all catalysts except calcium phosphate, the activity of which was halved.

6. None of the investigated catalysts underwent any change in crystal structure when compressed.

I am grateful to A. M. Rubinshtein for the X-ray analysis of the catalysts.

Received December 13, 1953.

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STABILIZATION OF α-HALO ETHERS

M. F. Shostakovsky and A. V. Bogdanova

The high reactivity of the α-halo ethers of general formula $CH_2 - CH\,Hal - OR$ (R = Alk or Ar), which have been previously synthesized and investigated by us [1, 2, 3], is being made use of to an increasing extent in the synthesis and investigation of various vinyl ether derivatives. A serious obstacle to the wider application of these compounds is their extreme instability in comparison with alkyl halomethyl ethers of formula $CH_2Hal - OAlk$ [4].

Experiments with many of these ethers have shown that decomposition of the initially pure ether sets in already after three hours in a sealed tube; after three weeks decomposition is complete. On this account we have carried out experiments on the stabilization of α-halo ethers, and, as a result, we have discovered conditions under which they may be kept for a long time. By use of this method of preservation it is no longer necessary to use all of a synthesized sample of α-halo ether immediately; it may be used a little at a time in a series of experiments.

α-Halo ethers can be readily preserved in the pure state at below 0°, but this method is inconvenient in practice, so that the most satisfactory method of preservation would appear to be one in which solvent stabilizers are used. The properties and reactions of α-halo ethers show [2, 3] that the bromo compounds are the least stable, and we therefore carried out most of our experiments on the selection of a solvent (stabilizer) with these ethers, on the assumption that a stabilizer suitable for α-bromo ethers would undoubtedly be suitable also for α-chloro ethers.

It has been noted previously [5] that the keeping of pure 1-bromoethyl butyl ether in diffused light at room temperature for three weeks is accompanied by its complete decomposition into butyl bromide and water. This decomposition of 1-bromoethyl butyl ether at room temperature in diffused light begins already after three hours. Our experiments have shown that an addition of only 15-20% of diethyl ether to 1-bromoethyl butyl ether enables it to be preserved at room temperature for two months or more.

1-Chloroethyl ethyl ether with an addition of 25% of diethyl ether was preserved in a sealed tube at room temperature for four years. It is interesting that, when the contents of the tube were distilled, apart from 1-chloroethyl ethyl ether, high-boiling products were isolated that were not only α-substituted, but also β-substituted. It may be supposed that acetal formation occurred, accompanied by the replacement of β-hydrogen atoms by chlorine atoms in a manner similar to the successive entry of chlorine into the α- and β-positions in the diethyl ether molecule [7, 8]. Satisfactory results were obtained also by the use of benzene and dioxane as solvent stabilizers: the keeping life of 1-bromoethyl butyl ether at room temperature in presence of 20% of these substances was more than one month.

α-Halo ethers are particularly sensitive to reaction at elevated temperatures [5, 6]. It has been shown [5] that heating of pure 1-bromoethyl butyl ether at 80-100° is accompanied by its complete decomposition, when it gives butyl bromide in 97.1% yield. Since most of the syntheses with α-halo ethers are carried out at elevated temperatures, it was of particular interest to find the conditions for the stabilization of α-halo ethers at such temperatures. By the use of the proposed solvent stabilizers it was found possible to preserve α-bromo ethers for more than one and a half months. The experiments showed that for the stabilization of α-halo ethers at elevated temperatures greater amounts of solvent stabilizer were required, as compared with that required at room temperature.

EXPERIMENTAL

The α-halo ethers used had the constants given in Table 1.

The following solvents were examined as stabilizers: dioxane, petroleum ether, benzene, diethyl ether. These substances were used in the absolute form. The change in the color of the solution of α-halo ether served as an outward sign of decomposition. By way of example we now cite a few experiments on the stabilization of α-halo ethers.

TABLE 1
Constants of α-Halo Ethers

Ether	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
1-Chloroethyl ethyl ether	34-35 (64)	1.4040	0.9493
1-Bromoethyl ethyl ether	40-41 (42)	1.4465	1.2770
1-Bromoethyl butyl ether	57-58 (10)	1.4485	1.2086

1. Stabilization of 1-Bromoethyl Butyl Ether at Room Temperature. 1-Bromoethyl butyl ether (3 g) and 0.5 g (17%) of the solvent stabilizer were sealed in a 10-ml tube. The tube was kept in diffused light at room temperature. The change in the color of the solution with time will be seen from Table 2.

TABLE 2
Change in the Color of Solutions of 1-Bromoethyl Butyl Ether kept at Room Temperature

Tube No.	Solvent stabilizer	Time of keeping	
		1 month	2 months
1	Benzene	Pink	Brown
2	Dioxane	Faintly pink	Brown
3	Diethyl ether	Colorless	Colorless

The contents of the tubes were vacuum-distilled, and yielded: Tube No. 3, 2.8 g of 1-bromoethyl butyl ether, b.p. 59-60° (12 mm); n_D^{20} 1.4480; d_4^{20} 1.2082. Each of Tube No. 1 and No. 2, 2.5 g of 1-bromoethyl butyl ether having the same constants as the starting material.

2. Stabilization of 1-Bromoethyl Butyl Ether at 60°. In each 10-ml tube, 3 g of 1-bromoethyl butyl ether and 3 g of solvent stabilizer were sealed, and the tubes were kept in diffused light at room temperature for two weeks, and were then placed in a thermostat and left there at 60° for five weeks. After the two weeks in diffused light at room temperature, all of the solutions remained colorless, and changes in color occurred only during storage at 60°, as shown in Table 3.

TABLE 3
Change in the Color of Solutions of 1-Bromoethyl Butyl Ether kept at 60°.

Tube No.	Solvent stabilizer	Time of keeping		
		1 day	4 weeks	5 weeks
1	Benzene	Slightly colored	Dark-colored	Black
2	Dioxane	Slightly colored	Dark-colored	Black
3	Diethyl ether	Colorless	Colorless	Dark-colored

The contents of the tubes were vacuum-fractionated, and yielded: Tube No. 3, 2.7 g of 1-bromoethyl butyl ether, b.p. 70-71.5° (22 mm), n_D^{20} 1.4478; d_4^{20} 1.2083. Tubes No. 1 and 2, 2.2 g and 2.5 g respectively of 1-bromoethyl butyl ether having the same constants as the starting material.

3. Stabilization of 1-Bromoethyl Ethyl Ether at Room Temperature. A mixture of 3 g of 1-bromoethyl ethyl ether and 0.5 g (17%) of solvent stabilizer was sealed in each tube, and the tubes were kept at room temperature in diffused light. The changes of color with time are indicated in Table 4.

TABLE 4
Change in Color of Solutions of 1-Bromoethyl Ethyl Ether kept at Room Temperature

Tube No.	Solvent stabilizer	Time of keeping	
		1 week	4 weeks
1	Dioxane	Colorless	Dark-colored
2	Petroleum ether	Pink	Dark-colored
3	Benzene	Yellow	Dark-colored
4	Diethyl ether	Colorless	Slightly pink

The contents of the tubes were vacuum-fractionated, and yielded:: Each of Tubes 1, 2, and 3, 2.5 g of 1-bromoethyl ethyl ether. Tube 4, 2.8 g of the ether. The constants of all of the samples of 1-bromoethyl ethyl ether recovered were identical with those of the starting material.

4. Stabilization of 1-Chloroethyl Ethyl Ether at Room Temperature. A mixture of 20 g of 1-chloroethyl ethyl ether and 5 ml (25%) of diethyl ether was sealed in a tube and kept at room temperature in diffused light. The tube was kept in the laboratory from November 29, 1948, to August 29, 1952. The contents became darker in color, but no precipitate formed. Vacuum fractionation yielded 7.5 g (38%) of 1-chloroethyl ethyl ether, b.p. 30-31.5° (61 mm); n_D^{20} 1.4040; d_4^{20} 0.9492. The higher-boiling fractions yielded 6.2 g of a product having the following constants: b.p. 71-72° (17 mm); n_D^{20} 1.4320; d_D^{20} 1.0432; Found MR 37.95; Calculated for acetaldehyde chloroethyl ethyl acetal MR 38.05

	Found M:	161.0, 163.8
$C_6H_{13}O_2Cl$	Calculated M:	152.62

Total Cl content (combustion)	29.65%
Cl^- content (titration)	11.9 %
H^+ content (titration with 0.1 N NaOH)	0.355%
H^+ content (Calculated from Cl^- content)	0.338%

This product was treated with dilute caustic soda, washed with water until neutral, and extracted with benzene. The extract was dried over $CaCl_2$, and the benzene was distilled off. Vacuum distillation of the residue yielded a fraction of b.p. 66-67° at 22 mm and n_D^{20} 1.4273. This substance did not have a sharp odor and gave no precipitate with silver nitrate, but it gave a positive Beilstein test for halogen. The chlorine content of this fraction (by combustion) was 17.68%.

Owing to the small amount of the substance isolated, it was unfortunately impossible to investigate it in greater detail, but the results obtained permit us to suppose that it consisted of a mixture of the 1- and 2-chloroethyl ethyl acetals of acetaldehyde.

SUMMARY

1. The conditions have been determined for the stabilization of α-halo ethers, so enabling them to be kept both at room and at elevated temperature.

2. An addition of 15-20% of diethyl ether to an α-halo ether stabilizes it at room temperature for a period of from two months to four years. Addition of 50% of diethyl ether enables α-halo ethers to be kept for two months at elevated temperatures.

Received October 21, 1952.

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** See Consultants Bureau Translation, page 1367.

*** See Consultants Bureau Translation, page 1379.

**** See Consultants Bureau Translation, page 429.

***** See Consultants Bureau Translation, page 435.

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REACTIONS BETWEEN VINYL COMPOUNDS AND MULTIFUNCTIONAL COMPOUNDS

COMMUNICATION 1. REACTIONS OF ALKYL VINYL ETHERS WITH GLYCEROL

M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya

This communication is the first of a series on our investigations on the reactions between various vinyl compounds of general formula $CH_2=CH-R$ (R may be OAlk, OR, OCOR, Hal, SR, NR_2, etc.) and various multifunctional compounds containing hydroxyl, carboxyl, and other functional groups.

The reactions between vinyl ethers and substances containing various functional groups provide a valuable method for the synthesis of a number of new compounds.

The course of the reaction between vinyl ethers and alcohols, phenols, acids, or other analogous compounds may be represented as follows:

$$CH_2=CH-OR + HOR' \longrightarrow CH_3-CH\begin{matrix}OR\\OR_1\end{matrix},$$

(R and R_1 may be alkyl, aryl, acyl, etc.).

These reactions are of interest not only from the point of view of synthesis, but also for the study of the properties and reactions of the original vinyl ethers and compounds containing a mobile hydrogen. Some considerable investigation has been made into the course of the reactions of alkyl vinyl ethers with monohydric alcohols having primary or secondary hydroxyl groups.

An investigation of the conditions under which polyhydric alcohols add to alkyl vinyl ethers was of particular interest. It is known from previous investigations by Shostakovsky and coworkers [1, 2, 3] that the addition products formed by monohydric alcohols with alkyl vinyl ethers are acetals of the following structures:

$$CH_3-CH\begin{matrix}OR\\OR\end{matrix} \quad \text{and} \quad CH_3-CH\begin{matrix}OR\\OR_1\end{matrix}$$

The structure (1) and disproportionation (2) of the acetals can be illustrated by the following schemes:

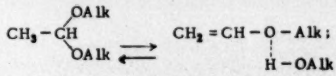
$$CH_3-CH\begin{matrix}OR\\OR\end{matrix} \rightleftharpoons CH_2=CH-O-R \quad (1)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad H-OR$$

$$2CH_3-CH\begin{matrix}OR\\OR_1\end{matrix} \longrightarrow CH_3-CH\begin{matrix}OR\\OR\end{matrix} + CH_3-CH\begin{matrix}OR_1\\OR_1\end{matrix} \quad (2)$$

The tautomerism of acetals results from the mobilities of hydrogen atoms, both the hydrogen of the methyl of the aldehyde residue and the hydrogen of the hydroxyl of the alcohol. An interesting special case is presented by mixed acetals containing both an alkoxyl and an aryloxyl radical:

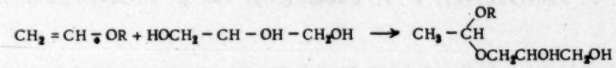
$$CH_3-CH\begin{matrix}OAlk\\OAr\end{matrix} \longrightarrow CH_2=CH-O-Alk$$
$$\qquad\qquad\qquad\qquad\qquad\quad H-O-Ar$$

Here equilibrium is greatly displaced to the right, owing to the fact that phenols contain hydrogen of greater mobility. Dialkyl acetals (in which the alkyls may be the same or different) also exist in two tautomeric forms:

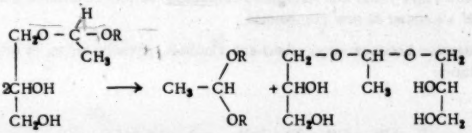


but in this case the point of equilibrium is different, being in the direction of the classical acetal structure.

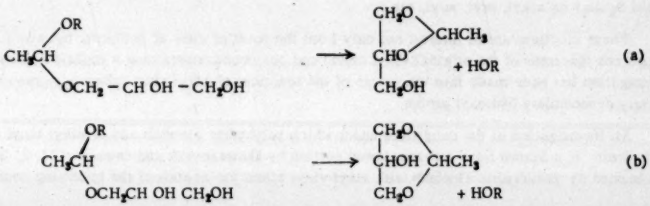
Particular interest is presented by the synthesis and reactions of acetals in which one alcohol residue is derived from a polyhydric alcohol, such as glycerol. When ethyl vinyl or ethyl butyl ether reacts with glycerol (equimolecular ratio of reactants), the first reaction should be as follows:



(R is C_2H_5 or C_4H_9). The resulting acetal may behave in two different ways, i.e., either undergo disproportionation according to the scheme:

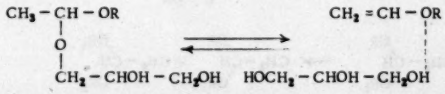


or undergo cyclization according to schemes (a) or (b):



It was found that in practice the rate of cyclization is greater than that of disproportionation. Our main products in the reaction of ethyl vinyl ether with glycerol were the 1,2 and 1,3 cyclic acetals of glycerol (which we shall refer to as 1,2- and 1,3-O-ethylideneglycerol respectively) and ethanol, only very small amounts of acetaldehyde diethyl acetal being obtained. In the reaction of butyl vinyl ether with glycerol, 1,2-O-ethylideneglycerol and butyl alcohol were isolated. The formation of only 1,2-O-ethylideneglycerol is evidently to be explained by the lower mobility of the alcohol radical of butyl vinyl ether.

The mechanism of the formation of mixed acetals of ethyl alcohol and glycerol can be represented as follows:

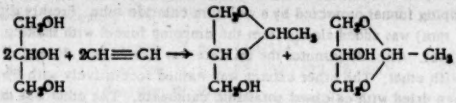


This is in its essence tautomerism. It is to be expected that the hydrogen bond will be formed at the expense of the more mobile hydrogen of one of the glycerol hydroxyl groups.

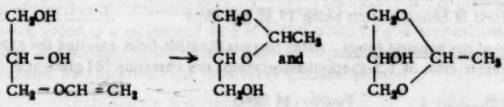
In the present investigation we have obtained twice as much 1,2-O-ethylideneglycerol as 1,3-O-ethylideneglycerol. This difference may result from the fact that, owing to its spatial proximity, the hydrogen of the 2-hydroxyl

group is the first to react, and is followed by the hydrogen of the 1-hydroxyl. These considerations relating to the displacement of alkoxyl groups from mixed acetals by free hydroxyls of glycerol are fully in accord with previous investigations of one of us and coworkers [4].

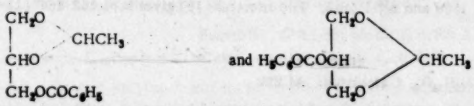
Nieuwland and coworkers [5, 6] have obtained 1,2- and 1,3-O-ethylideneglycerols by the reaction of glycerol with acetylene in presence of HgO and BF_3:



Shostakovsky and Gracheva [7] have prepared the same acetals by the cyclization of glycerol monovinyl ether under the action of heat and traces of mineral acid:



In the present work we have shown that unsymmetrical mixed acetals containing alkoxyl groups and free hydroxyls derived from glycerol undergo cyclization as a result of interaction between the alkoxyl group and one of the hydroxyls of the glycerol, an alcohol being eliminated and the corresponding cyclic acetal formed. The separation of the resulting isomeric acetals was effected by the aid of benzoylation, the compounds



being isolated; their hydrolysis products corresponded in constants to 1,2- and 1,3-O-ethylideneglycerols.

EXPERIMENTAL

Starting Materials: The alkyl vinyl ethers were prepared by Favorsky and Shostakovsky's method; ethyl vinyl ether, b.p. 35-36°; n_D^{20} 1.3782; d_4^{20} 1.7533; butyl vinyl ether, b.p. 92-93°; n_D^{20} 1.4030; d_4^{20} 0.7795; glycerol had b.p. 164-172° (8-14 mm); n_D^{20} 1.4728; d_4^{20} 1.2582.

Reaction of Ethyl Vinyl Ether with Glycerol

A mixture of 14.4 g (0.2 mole) of ethyl vinyl ether and 18.4 g (0.2 mole) of glycerol was placed in a three-necked flask fitted with mercury-sealed stirrer, condenser, and thermometer. It was then stirred for 30 minutes, when one drop (0.014 g of HCl) of catalyst was added. In the course of 30 minutes the temperature gradually rose from 23° to 35°, and then rose sharply to 76.5°. The reaction yielded 31.9 g of product.

The reaction mixture was neutralized with potassium carbonate and distilled from a Favorsky flask. From 29.03 g the following fractions were obtained

Fraction I	b.p. 76-77°; 7.5 g
Fraction II	b.p. 76-93° (11-12 mm); 17.8 g
Residue	3.4 g

a) Investigation of Fraction I. The fraction smelled of acetal, but reacted vigorously with sodium. Agulhon's qualitative test [8] on a trial sample gave a color, almost the same in intensity as that obtained in a parallel test on pure ethyl alcohol. The constants of the fraction (n_D^{20} 1.3660 and d_4^{20} 1.7980) and qualitative tests all indicated that Fraction I consisted essentially of ethyl alcohol containing some acetaldehyde diethyl acetal, the separation of which did not appear to be possible. For ethyl alcohol the literature gives n_D^{20} 1.361 and d_4^{20} 0.789. The yield of the fraction, regarded as ethyl alcohol, was 92.5%.

b) Investigation of Fraction II. Fraction II had the following constants: n_D^{20} 1.4448; d_4^{20} 1.1260. A second fractionation under reduced pressure did not give any clear resolution of the product. It was found to contain free hydroxyl groups.

In order to resolve Fraction II it was benzoylated. A mixture of the fraction (15 g; dried with potassium carbonate) with 36 g of pyridine (dehydrated and distilled over BaO; b.p. 114-115°) was placed in a flask, which was closed with a stopper carrying a dropping funnel protected by a calcium chloride tube. Freshly distilled benzoyl chloride (15 g; b.p. 75-76° at 10-11 mm) was added slowly from the dropping funnel with shaking. Reaction was accompanied by evolution of much heat. After 30 minutes the mixture was poured into 300 ml of distilled water, and the oily product was extracted with ether. The ether extract was washed successively with 5% KOH, 3% H_2SO_4, and water (until neutral), and was then dried with calcined potassium carbonate. The ether was driven off, and the oil that remained behind was heated at 100° in a vacuum to remove traces of pyridine. To this mixture of benzoic esters 30 ml of gasoline (b.p. 50-60°) was added, and the solution was cooled to −12°. The crystals that were then precipitated were filtered off through a cooled funnel, and the liquid benzoic ester remaining after removal of gasoline was vacuum-distilled. In this way 5.9 g of crystalline benzoic ester and 11.36 g of liquid benzoic ester were obtained, the total yield of benzoic esters being 17.26 g (61%).

c) Characterization of the Benzoic Esters. After recrystallization from gasoline the crystalline benzoic ester melted at 85°. For the benzoic ester of 1,3-O-ethylideneglycerol the literature [6] gives m.p. 86°.

Found: M 224.1
$C_{12}H_{14}O_4$ Calculated: M 222 *

Found %: C 64.54; 64.76; H 6.48; 6.46
$C_{12}H_{14}O_4$ Calculated %: C 64.83; H 6.31

After a second freezing treatment and redistillation, the liquid benzoic ester had the following constants: b.p. 161-162° (9-10 mm); d_4^{20} 1.1558 and n_D^{20} 1.5140. The literature [6] gives b.p. 163-164° (11-12 mm); n_D^{17} 1.5145; d_4^{17} 1.1618.

Found: M 220
$C_{12}H_{14}O_4$. Calculated: M 222

Found %: C 65.87; 64.63; H 6.41; 6.46
$C_{12}H_{14}O_4$. Calculated %: C 64.83; H 6.31

Preparation of 1,3-O-Ethylideneglycerol by Hydrolysis of its Benzoic Ester

The crystalline 1,3-O-ethylideneglycerol benzoic ester (2.2 g; m.p. 85°) was heated and stirred with 15 ml of 10% KOH until solution was complete. To the clear cooled solution 8 g of calcined potassium carbonate was added, and it was then subjected to repeated extraction with ether. The ether extract was dried with calcined potassium carbonate, and the ether was distilled off, yielding 0.41 g (38%) of product, b.p. 66-68° (11-12 mm); n_D^{20} 1.4520; $n_D^{16.5}$ 1.4538. For 1,3-O-ethylideneglycerol the literature [6] gives b.p. 52° (2 mm); n_D^{17} 1.4532.

Found %: C 50.81; 50.95; H 8.81; 8.77
$C_5H_{10}O_3$. Calculated %: C 50.84; H 8.47

Preparation of 1,2-O-Ethylideneglycerol by Hydrolysis of its Benzoic Ester

The liquid ethylideneglycerol (8.06 g), treated in a similar way, yielded 1.74 g (43%) of a product of b.p. 84-85° (11-12 mm); n_D^{20} 1.4436. For 1,2-O-ethylideneglycerol the literature [6] gives b.p. 68-70° (1 mm); n_D^{17} 1.4415; d_4^{17} 1.1248.

Found %: C 50.34; 50.14; H 8.61; 8.51
$C_5H_{10}O_3$. Calculated %: C 50.84 H 8.47

When 3 moles of ethyl vinyl ether reacted with 1 mole of glycerol, no 1,2- or 1,3-O-ethylideneglycerol was isolated. The reaction products were ethyl alcohol, acetaldehyde diethyl acetal, and bisethylideneglycerol. Study of these reaction products continues.

Reaction of Butyl Vinyl Ether with Glycerol

A mixture of 25.04 g (0.25 mole) of butyl vinyl ether and 23 g (0.25 mole) of glycerol was stirred as in the previous experiment for 30 minutes. Catalyst was added (3 drops, i.e., 0.042 g, of HCl), but no rise of temperature

* The molecular weight was determined by the Rast-Munster method.

was observed after one hour; the mixture was, therefore, heated to 50°. After 30 minutes at 50° rise in temperature was observed, 61° being attained in five minutes in absence of applied heat. The emulsion formed by the reactants was converted into a homogeneous clear solution, and when this occurred there was an immediate fall in temperature by 5° (to 56°). The reaction yielded 47.72 g of product.

The reaction product was neutralized with potassium carbonate and distilled from a Favorsky flask, when 45 g yielded the following fractions:

Fraction I, b.p. 113-114°;	16.9 g; n_D^{20} 1.4120
Fraction II, b.p. 95-103°; (23-25 mm):	23.01 g; n_D^{20} 1.4368
Fraction III, Residue	3.13 g; n_D^{20} 1.4755

a) Investigation of Fraction I. Fraction I reacted vigorously with sodium. Redistillation yielded 11.87 g (64.2%) of a product of b.p. 116-117°; n_D^{20} 1.4030; d_4^{20} 0.8232, having the characteristic odor of butyl alcohol. Agulhon's test [8] was positive for alcohol. For butyl alcohol the literature gives b.p. 117.7°; d_4^{20} 0.810; n_D^{20} 1.3993.

b) Investigation of Fraction II. Fraction II, boiling range 95-103° at 23-25 mm, n_D^{20} 1.4368, was benzolated 20 g of the fraction being added to a mixture of 48 g of pyridine and 24 g of benzoyl chloride. When treated as described above (cooling of a solution of the benzoic ester in 50 ml of gasoline), no precipitate of a crystalline product was obtained. Vacuum fractionation after removal of gasoline yielded:

Fraction I, b.p. 100-152° (12 mm):	8.18 g; n_D^{20} 1.5072
Fraction II, b.p. 160-161° (12 mm):	29.98 g; n_D^{20} 1.5152
Fraction III, Residue	2.12 g; n_D^{20} 1.5268

Fraction I was redistilled and yielded a product boiling at 90 - 118° (10 - 11 mm); n_D^{20} 1.5052, which appeared to be butyl benzoate. Redistillation of Fraction II yielded a product of b.p. 159 - 160° (10 mm); n_D^{20} 1.5143; d_D^{20} 1.1617, corresponding in constants to the benzoic ester of 1,2-O-ethylideneglycerol.

Found %: C 64.98; 65.15; H 6.39; 6.48

$C_{12}H_{14}O$. Calculated %: C 66.05; H 6.31

Hydrolysis of this substance yielded a product of b.p. 76 - 78° (9 - 10 mm); n_D^{20} 1.4435; d_4^{20} 1.1265, corresponding to 1,2-O-ethylideneglycerol. From 7.50 g of benzoic ester taken for hydrolysis, 3.09 (g) (77.63%) of 1,2-O-ethylideneglycerol was obtained.

SUMMARY

1. A study has been made of the reactions of ethyl vinyl ether and of butyl vinyl ether with glycerol in presence of traces of hydrogen chloride, the reactants being taken in equimolecular proportions. The main reaction products were 1,2- and 1,3-O-ethylidineglycerol from ethyl vinyl ether and 1,2-O-ethylideneglycerol from butyl vinyl ether. 2. The formation of 1,2- and 1,3-O-ethylideneglycerols from ethyl vinyl ether and glycerol, and also of 1,2-O-ethylideneglycerol from butyl vinyl ether and glycerol, evidently proceeds via the formation of the corresponding mixed acetal, which then undergoes cyclization.

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Institute of Organic Chemistry
of the U.S.S.R. Academy of Sciences
Received November 19, 1952.

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BRIEF COMMUNICATIONS

SYNTHESIS OF 1-METHYL-3-PROPYLCYCLOBUTANE

B. A. Kazansky and M. Yu. Lukina

1-Methyl-3-propylcyclobutane was synthesized by the method that we have used previously for 1,3-dimethyl- and 1-ethyl-3-methyl-cyclobutane [1, 2]. It was obtained as a mixture of geometric isomers and was distilled through a 60-plate column. The two fractions, b.p. 116.1-116.3° and 118.5-118.7° (760 mm), consisted respectively of the trans and cis forms, neither being completely free from the other stereoisomer owing to the closeness of their boiling points. The results given in this note relating to their constants are therefore of a tentative character.

EXPERIMENTAL

Ethyl 3-methylcyclobutyl ketone, prepared from 3-methylcyclobutanecarboxylic acid and propionic acid by the procedure described in previous papers [1, 2], had the following constants: b.p. 164-170° (753.0 mm); n_D^{20} 1.4332; d_4^{20} 0.8757; found MR 37.44; calculated for $C_8H_{14}O$ MR 36.95; ε MR 0.49.

Found %: C 75.88; 75.82; H 11.13; 11.10
$C_8H_{14}O$. Calculated %: C 76.11; H 11.19

The semicarbazone of ethyl 3-methylcyclobutyl ketone was prepared by Zelinsky's method [3], and was recrystallized from aqueous methanol. After four recrystallizations it melted at 130-131.2°.

Found %: N 22.75; 22.75
$C_9H_{17}N_3O$. Calculated %: N 23.03

A mixture of 32 g (0.5 mole) of 85% hydrazine hydrate and 30 ml of alcohol was added slowly with stirring to a solution of 31.5 g (0.25 mole) of ethyl 3-methylcyclobutyl ketone in 35 ml of redistilled ethyl alcohol. The mixture was boiled for four hours under reflux. The alcohol and excess of hydrazine hydrate were distilled off (oil bath), the bath temperature being above 140°. The reaction mass was cooled, and a small amount of solid caustic soda was added, the water layer being then removed in a separating funnel. The hydrazone, carefully dried with caustic potash, boiled at 104-110° at 115 mm. The decomposition was carried out as usual in a Favorsky flask, attached through a condenser to a receiver and well cooled trap in the form of a coil. For the decomposition caustic potash fused in a silver dish was used; no platinum catalyst was added to the alkali in this work.

The mixture of hydrocarbon and unchanged hydrazone was again subjected to the decomposition treatment over a fresh portion of fused caustic alkali. The hydrocarbon was then washed successively with water, 50% acetic acid, 50% sulfuric acid, water, 25% caustic soda, and again water. The yield of hydrocarbon (dried with fused calcium chloride) was 16.0 g (57.1% on the ketone). In three experiments 33.7 g of hydrocarbon was obtained altogether.

The product, a mixture of cis and trans isomers, was distilled through a 60-plate column. The amount taken was 33.7 g (45 ml), and when 34.0 ml had been distilled over, 10 ml of redistilled decahydronaphthalene was added, thus enabling the higher-boiling isomer to be brought over. Distillation was at a reflux number of 50. Cuts of range 116.1-116.3° and 118.5-118.7° were taken, together with intermediate cuts. On the basis of the Auwers-Skita rule [4, 5] we assumed that the fraction of b.p. 116.1-116.3° corresponded to the trans form, and the fraction of b.p. 118.5-118.7° to the cis form of 1-methyl-3-propylcyclobutane. The properties of the stereoisomers are as follows:

trans-1-Methyl-3-propylcyclobutane: b.p. 116.1-116.3° (760 mm); n_D^{20} 1.4088; d_4^{20} 0.7370; found MR 37.60; calculated for C_8H_{16} MR 36.94; ε MR 0.66; aniline point 60.4°.

Found %: C 85.43; 85.50; H 14.38; 14.48
C_8H_{16}. Calculated %: C 85.61; H 14.39

cis-1-Methyl-3-propylcyclobutane: b.p. 118.5-118.7° (760 mm); n_D^{20} 1.4128; d_4^{20} 0.7453; found MR 37.49; calculated for C_8H_{16} MR 36.94; ε MR 0.55; aniline point 57.2°.

Found %: C 85.51; 85.30; H 14.57; 14.70
C_8H_{16}. Calculated %: C 85.61; H 14.39

SUMMARY

1. 1-Methyl-3-propylcyclobutane has been prepared for the first time.
2. Some new disubstituted cyclobutanes have been prepared and characterized.

Received November 13, 1953

Institute of Organic Chemistry
of the USSR Academy of Sciences

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SYNTHESIS AND REACTIONS OF UNSATURATED ORGANOSILICON COMPOUNDS

COMMUNICATION 1. SYNTHESIS OF VINYLCHLOROSILANES BY THE DIRECT METHOD

M. F. Shostakovsky and D. A. Kochkin

Unsaturated organosilicon compounds are of great theoretical interest and form a rich source for a great variety of syntheses. In this communication we describe conditions for the synthesis of vinylhalosilanes of general formula $(CH_2=CH)_nSiX_{4-n}$, in which X is a halogen (chlorine, bromine, fluorine). The example we have taken for study is the synthesis of vinylchlorosilanes. Until now the study of the synthesis of compounds of this type has been inadequate. References to methods for the preparation of unsaturated organosilicon compounds are mainly concerned with methods for their preparation with the aid of organomagnesium compounds [1-4, 6]. Attempts to prepare vinylchlorosilanes by direct synthesis from vinyl chloride and metallic silicon have not been successful [5].

Several variants are possible in the direct method for the preparation of vinylchlorosilanes, and the simplest of these appears to be the reaction of vinyl chloride with metallic silicon.

We have investigated the conditions for the direct synthesis of vinylchlorosilanes from vinyl chloride and copper-silicon alloys. In the course of these investigations we established the possibility of obtaining vinylchlorosilanes by passage of vinyl chloride over a copper-silicon alloy (20: 80) at 350-400°. The scheme of reactions can be represented by the following equations:

$$4CH_2=CHCl + Si \rightarrow SiCl_4 + 8C + 6H_2. \quad (1)$$

$$3CH_2=CHCl + Si \rightarrow CH_2=CHSiCl_3 + 4C + 3H_2. \quad (2)$$

$$2CH_2=CHCl + Si \rightarrow (CH_2=CH)_2SiCl_2. \quad (3)$$

$$3CH_2=CHCl + 2Si \rightarrow CH_2=CHSiHCl_2 + CH_2=CHSiH_2Cl + 2C. \quad (4)$$

Reaction proceeds with preferential formation of trichlorovinylsilane and dichlorodivinylsilane in 35% yield. Among undesirable side reactions we may note the formation of silicon tetrachloride and a considerable amount of charcoal, resulting in great losses of vinyl chloride. Reaction proceeds with evolution of much heat; it is not very smooth.

EXPERIMENTAL

Copper-silicon alloy (20: 80; 1.5 kg) in the form of 10-15-mm pieces was loaded into an iron tube, diameter 50 mm and length 1000 mm, fitted with two metal tubes for thermometer and wire stirrer. The loaded tube was placed in an electrically heated tubular muffle and heated to 350-400°. In order to dry out the alloy, dry nitrogen was passed at that temperature for 50 minutes at 1.0 liter per minute. Vinyl chloride was then passed at 0.1 liter per minute. As the synthesis proceeded, an irregular distribution of temperature in the contact mass was observed; this behavior was a result of the highly exothermic nature of the reaction, and it led to coke formation at various places in the reaction tube. In order to prevent excessive coking, it was necessary to stir. The reaction was continued for 80 hours, 480 liters of vinyl chloride being passed. The products of the synthesis (750 g) contained 70.5-71.0% of chloride ion; they contained 45-48% of trichlorovinylsilane and dichlorodivinylsilane. The crude products of the synthesis were fractionated through a two-meter column, diameter 18 mm and having a porcelain filling. The following main fractions were obtained:

Fraction I, b.p. 56-60°, yield 30.5%
Fraction II, b.p. 90-94°, yield 32.5%
Fraction III, b.p. 116-120°, yield 9.3%

Fraction II, b.p. 90-94°, was refractionated, and a fraction of b.p. 92.5-94.0° (752 mm); d_4^{20} 1.2650, was collected. It analyzed as follows:

Found %: Si 17.60; Cl 65.03
$C_2H_3SiCl_3$. Calculated %: Si 17.37; Cl 65.89

The molecular weight, determined cryoscopically in benzene, was 162.73; calculated for $C_2H_3SiCl_3$ 161.58. These results correspond to trichlorovinylsilane [7]. The yield of trichlorovinylsilane was 20.3% on the vinyl chloride taken.

Fraction III, b.p. 116-120°, was refractionated, and a fraction of b.p. 118-119° (754 mm); d_4^{20} 1.0813 was collected. It analyzed as follows:

Found %: Si 17.83; Cl 47.00
$C_4H_6SiCl_2$. Calculated %: Si 18.34; Cl 46.30

These results show that the fraction of b.p. 118-119° is essentially dichlorodivinylsilane [7], the properties and yield of which we are now studying.

Received November 12, 1953

Institute of Organic Chemistry of
the USSR Academy of Sciences

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* See Consultants Bureau Translation, page a-425
** " " " " " 1507

DISCUSSION

EXPERIMENTAL DETERMINATION OF ELECTRON DENSITY IN CRYSTALS*

N. V. Ageev

There can be no doubt about the enormous significance for contemporary science of the development of the theory of the structure of substances. The development of this theory is possible only by the accumulation of experimental facts on the basis of which the fundamental principles of theory can be developed. The theoretical principles so created at the same time require experimental verification and confirmation.

It will be seen from this that the development of experimental methods for the determination of the nature of the chemical bond in crystalline substances is of the highest importance. One of these methods is the determination of electron density. It would have been expected that this method would have drawn the attention of specialists and would have been developed in detail so that it might be used for the solution of problems concerning the nature of the chemical bond in crystalline substances. Actually, however, this method has been recently subjected to unmerited attacks, without being examined in a proper critical manner.

History of the Subject

We shall discuss briefly the history of the experimental determination of electron density. The method was first proposed by Bragg [1] in 1915 for the solution of questions of a purely structural nature, namely, the determination of the centers of gravity of atoms in a lattice, which correspond to maxima of electron density. The use of this method for structural purposes is now very extensive. Further development of this method resulted from Duane's work [2], in which the application of Fourier series for the calculation of electron density was greatly simplified.

The first experimental investigations on the distribution of electron density were carried out by Havinghurst [3] in 1925-1927 for sodium chloride, sodium fluoride, and lithium fluoride crystals. This method was later applied by Wollan [4] in 1930 for magnesium oxide, and by Grimm, Brill, Hermann, and Peters [5] in 1938-1944 for sodium chloride, diamond, hexamethylenetetramine, magnesium, and aluminum.

In the Soviet Union the first investigations on the determination of electron density were begun in 1940 by Breger and Zhdanov [6], who studied the nature of the chemical bond in graphite and boron nitride. In the years 1945-1952 systematic studies were made by Ageev, Guseva, and Ageeva [7-12] of the electron density in aluminum, copper, nickel, and the compounds NiAl and Mg_2Si. Finally, in 1948 Kritskaya and Rovinsky [13] obtained data for copper.

Method of Determining Electron Density

Before passing to an examination of the critical remarks that have appeared recently (1951-1952) with respect to my investigations, I must discuss the essentials of the method used for the determination of electron density. The work of determining electron density can be divided into two parts: 1) determination of the experimental value of the atomic scattering factor for X-rays (f-curve) from a study of the intensity of reflected X-rays; and 2) calculation of the electron density in different directions of the crystal lattice by means of the triple Fourier series, the coefficients of which are values of the atomic scattering factor.

Determination of the f-Curve. The most laborious part of the investigation is the experimental part, which demands a series of carefully performed experiments, the accumulation of a large amount of experimental material, and very careful treatment and critical evaluation. The following two conditions must be observed so that the experimental f-curve can be used for calculation of the electron density. First, it is necessary to make sure that individual values of f are determined with sufficient accuracy. On this accuracy the accuracy of the electron density distribution curve mainly depends. This accuracy is determined by a number of experimental conditions, which are well known. The determination of f-curves, in its relation to experimental procedure and the effect of various factors on the experimental error, has been studied by a number of authors.

* Paper read before the Section of Physicochemical Analysis of the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR, April 22, 1953, Moscow.

In our investigations we have used the photographic method for the determination of X-ray intensities; we have used this method previously in the study of disorder-order transitions in solid solutions; and it has been used also by a number of authors for the determination of f-curves. In the investigations of Grimm, Brill, Hermann, and Peters [5] an ionization method was used for the measurement of intensities. In the determination of intensities for the construction of f-curves, both methods, photographic and ionization, are practically equivalent in value. No difficulties have been found as yet in the accurate measurement of intensities by either of these methods, and the errors in measurement associated with these methods are sufficiently small to be neglected in view of the fact that errors of another kind are undoubtedly of greater importance in the determination of f-curves.

For the measurement of X-ray intensities, the choice of the form and state of the material under investigation is of importance. We take finely crystalline samples of the material, since extinction, which is difficult to take into account in large crystals, can be completely eliminated in sufficiently fine crystals. Extinction is almost completely absent in aluminum and other substances that have been investigated so long as the size of the crystals is of the order of 10^{-5} cm. Considerable difficulties are met in the preparation of such samples. We have used three methods for these preparations: 1)films of aluminum and copper wereprepared by condensation of vapor in high vacuum; 2) nickel powder was prepared by reduction of the oxide with hydrogen; 3) powders of the compounds NiAl and Mg_2Si were prepared by grinding in an agate mortar. In all cases the powders were passed through a sieve having 200 mesh per inch, and washed with toluene. The particles of the powder were measured in a measuring microscope; they were of the order of 3-6 x 10^{-4} cm. Control X-ray studies of the powders after suitable thermal treatment enabled us in all cases to show that strains were absent and that the grain size was of the required order. The preparation of a suitable sample is the most vital and difficult part of the problem of determining f-curves.

For our X-ray studies we used samples both of flat and of cylindrical form. Use of the flat form permits the absorption factor to be determined relatively simply. Cylindrical samples were used in the determination of weak lines of low and closely arrayed values of θ; and they were not more than 0.2-0.3 mm in diameter, so that it was possible to take absorption into account. The X-ray photographs were taken and developed by the usual methods, care being taken to maintain conditions constant. A blackening curve was obtained for the photographic film used, and this was used in selecting the exposure and development conditions. The conversion from relative to absolute values of the atomic scattering factor was carried out by the method of substitution by a standard substance, usually aluminum, in a special camera.

The calculation of the electron density will be as complete as possible if the number of terms of the series is infinitely great. In practice it is possible to limit oneself to a finite number of terms, for experimental results obtained with a definite degree of accuracy do not permit the low amplitudes of Fourier terms of high order to be taken into account. It is, therefore, necessary to find the sum of a number of terms of the series, such that the last of these terms corresponds to the accuracy of the only experimentally determined quantity—the atomic scattering factor. The value of the atomic scattering factor of aluminum can now be determined accurate within $\pm$ 0.05. The number of terms must be taken so that the coefficients of the last of them are equal to this error. The number of terms obtained in the Fourier series will depend on the number of reflections obtained on the X-ray photograph, and this will depend on the wavelength of the radiation used. For example, for aluminum the use of FeK_α radiation will enable 64 terms to be obtained, the use of CuK_α will give 136 terms, and the use of MoK_α will give 698 terms. The atomic scattering factor for the last terms of the series will be 5.69 for FeK_α, 3.26 for CuK_α, and 0.85 for MoK_α. Hence, even the use of hard molybdenum radiation cannot lead to sufficiently low amplitudes in the last terms of the series. The error introduced into the calculation of electron density by this limitation of the number of the terms in the series has been called the "finite series error". It becomes greater as the radiation used becomes softer, and it can introduce considerable errors in the determination of electron density.

Calculation of Electron Density. The experimentally obtained f-curve can be used to calculate the distribution of electron density in the crystal lattice. The electron density in the crystal is a continuous periodic function of the spatial coordinates, and can be regarded as a function of one or of two coordinates, leading to a one-dimensional or two-dimensional series, i.e., to a projection of the electron-density distribution on a direction or plane in the crystal lattice. Both of these cases are of limited application, since it is not always possible to choose directions in the crystal so that projections of electron density do not overlap and only atoms of one sort are projected at each point. When we treat electron density as a function of three coordinates, we obtain a three-dimensional series characterizing the spatial distribution of electron density. For the calculation of the spatial distribution of electron density a triple Fourier series of the following form is used:

$$\rho_{xyz} = \sum_{h} \sum_{k=-\infty}^{+\infty} \sum_{l} A_{hkl} \cdot \cos 2\pi \left(h\frac{x}{a_1} + k\frac{y}{a_2} + l\frac{z}{a_3} \right),$$

(h, k, l are numberical indices varying from $+\infty$ to $-\infty$; a is the lattice constant; A_{hkl}, the Fourier series coefficient, is given by $A_{hkl} = \frac{1}{V} \cdot f_{hkl}$, in which V is the volume of the elementary cell; f is the atomic scattering factor, obtained from the experimentally determined f-curve). The zero term is calculated from the condition $f_0 = z$ (z is the total number of electrons in the atom). The only difficulty in the calculation of electron density is the "finite series error", which, as already indicated, cannot be eliminated by experimental methods; it can be eliminated only by calculation methods.

One of these methods consists in lengthening the experimentally found f-curve in the direction of greater values of $\sin\theta/\lambda$ by the extrapolation method proposed by Froman. This method cannot be regarded as sufficiently reliable, since the curve is continued beyond the limits of experimentally determined values of f and cannot be checked experimentally; also, the lengthening of the f-curve leads to a considerable increase in the number of Fourier terms and makes the task of summation much more difficult.

A second method was proposed by Grimm, Brill, Hermann, and Peters [5] under the name of the "calculation temperature" method; it consists in mathematical treatment of the amplitudes of the Fourier series so that the values of the last of them shall not be greater than the error in the experimentally determined atomic scattering factor. The mathematical treatment consists in multiplication of the atomic scattering factors by a temperature factor which adjusts the f-curve to a definite "calculation temperature". The error so introduced into the determination of electron density can be determined only by calculation. Calculations of this sort have been made by Hermann [5] in 1940, Kritskaya and Rovinsky [13] in 1948, and Ageev and Ageeva [8] in 1948.

Finally, we must refer to the mixed method proposed by Kritskaya and Rovinsky in 1948 [13], in which, on the one hand, the f-curve is somewhat lengthened by calculation by Hartree's method, and, on the other hand, this partly experimental and partly theoretical curve is adjusted to the calculation temperature by the method of Grimm and coworkers [5]. This mixed method has all of the errors of the two methods that we have examined, and has no advantages over them.

Significance of the Results Obtained

Among the results derived from experimental studies of electron density, the most interesting and important are not those which merely confirm what was known before this method of investigating the chemical bond was used, but those which yield new, previously unknown facts; these facts include:

1. The presence of "bridges" of electron density (homopolar bond), which unite chlorine atoms in ionic lattices of the sodium chloride type.

2. The presence of "bridges" of electron density in lattices of the diamond type having directed homopolar bonds in the directions of the lines joing the atoms (110 direction).

3. The presence of "bridges" between individual molecules in the molecular-type lattices of organic compounds (hexamethylenetetramine, oxalic acid).

4. Determination of the positions of hydrogen atoms in the lattices of organic compounds (hexamethylenetetramine).

5. The presence of irregular electron distribution and "bridges" in metal lattices (magnesium, copper, nickel).

6. The presence of incomplete ionization in metal lattices (aluminum).

7. The presence of "bridges" of electron density of various intensities (characteristic of the strength of the bond) between various atoms of the complex lattices of metallic compounds (NiAl, Mg_2Si).

8. The presence of asymmetrical deformation of the electron envelopes of atoms in the lattice of the metallic compound Mg_2Si.

These facts are of undoubted interest for the development of the theory of the structure of substances, and they permit a number of general inferences to be drawn.

The crystal structures of even the most simple substances are complex with respect to the nature of the chemical bonds present, and chemical bonds of a saturated type rarely exist in crystals. An examination of the distribution of electron density indicates the complex nature of the chemical bond in simple substances (sodium chloride, magnesium, copper, nickel). In no case is it possible to regard the complex chemical bond in a crystal as the simple sum of elementary types of chemical bonds. A knowledge of the distribution of electron density in crystals permits us to construct a model of the continuous change of the valency state of atoms in crystal lattices.

Reply to Criticisms

The first criticism of the method of determining electron density with the aid of Fourier series was made by Konobeevsky [14] in 1951. The essence of this criticism is as follows:

1. "The practical necessity of prematurely terminating the series, which is a result of the limited nature and slow extinction of the X-ray diffraction spectrum, has led to the idea of introducing an artificial factor that falls as the value of n increases, and this is equivalent to the introduction of an element of indefiniteness into the position of diffraction spectra [7-9, 5]. This will clearly distort the actual distribution to such a great extent [3, 13] that the method becomes of doubtful value."

2. "However, even if the summation could be performed quite correctly, the result could not be regarded as satisfactory in itself, for, in order to draw any conclusion from it that would have physical significance, it would be necessary by some method or other to separate the individual atoms from the distribution obtained. No theoretically based rules are known whereby this process could be effected."

On a number of occasions doubt concerning the electron-density method has been expressed by Boky [15], who has stated: "There are yet no direct and sufficiently accurate methods for the determination of electron density in the outer parts of molecules, although there is a direct and adequately accurate method for the determination of the positions of atoms in molecules."

Finally, in 1951 a paper by Snow [16] appeared in which a critical examination was made of six papers by me and my coworkers on the determination of electron density. The following points are advanced:

1. "In view of the extremely large artificial temperature factors used by Ageev and Ageeva, it is quite possible that the electron densities of the outermost electrons are increased somewhat and, therefore, at a point midway between nearest neighbors, even for truly spherically symmetrical atoms, there will appear an increase in electron density which may seem to be due to bridge bonds, but which will actually be caused by the summation of the overlapping density distributions of the outer electrons of the spherical atoms .... The 'bridges' found may, therefore, be entirely due to the method of calculation used by Ageev."

2. "It seems overly optimistic to place any reliance on an electron-density difference of 0.04 e/A^3 as being meaningful, or to suppose that anything very valid can be said about the valence of metallic aluminum no matter how the data are mathematically treated."

3. "Ageev and co-authors' choice of radiation for the work on copper, nickel and AlNi is particularly unfortunate, since the dispersion corrections are large for the long-wavelength radiations used, and the uncertainties in these corrections are large enough easily to mask the differences in intensity of low-order reflections due to the outer electron distribution."

In 1952 Konobeevsky [17] stated in a paper read at a conference on the theory of alloys:

1. "It has been proposed that an ever-decreasing factor should be introduced into the series, which is equivalent, in many cases, to the introduction of a very significant conventional temperature. This method not only permits one to manage with a comparatively small number of interferences, but also avoids calculation errors associated with the appearance of a "finite-series wave". It is not clear, however, whether the dwindling of the factor is not accompanied by the disappearance of essential variations in the distribution that is being analyzed. It must be pointed out also that fine differences in electron-distribution curves, representing various peculiarities of chemical bonds, are revealed in the form of still finer variations in structural amplitudes. This demands very careful measurement of X-ray interferences and the taking of all factors that may affect the intensity (extinction, absorption, etc.) into consideration."

2. "Difficulties arise also in the interpretation of the resulting projections or cross sections of electron density. Thus, N. V. Ageev treats the increase in density between two neighboring atoms of a metallic crystal as a manifestation of the presence of a special electron "bridge" corresponding to particularly strongly directed bonds. This effect, however, can be treated also as the simple superposition of the electron envelopes of two neighboring atoms."

3. "The method by which the number of free electrons in the crystal is calculated is a very doubtful one .... It is completely arbitrary, and therefore, many results obtained by its aid are, as we shall show below, incorrect."

All these criticisms center around the following points:

1. The effect of the temperature factor on the picture obtained of the electron-density distribution, including the "bridges".

2. The interpretation of the "bridges" of increased electron density.

3. The possibility of determining the degree of ionization of atoms in metal crystals on the basis of the picture of electron-density distribution.

4. The experimental conditions, and the errors that depend on them.

We shall now reply to these criticisms.

1. The effect of the temperature correction on the resulting picture of electron-density distribution was examined by us for the case of aluminum. Our calculations showed that the temperature correction affected mainly the position of the maximum of electron density at the point corresponding to the crystal lattice point. There were no changes at all in the electron density at points sufficiently far removed from the lattice points, i.e., lying in the interionic space. The only exceptions were values of electron density calculated without introduction of a "calculation temperature" or by use of a low value of this temperature, when the finite series error was significant. Already at a "calculation temperature" of 500°, there is no change in the electron-density distribution in the interionic space, in which the valency electrons that are of interest for us are to be found.

Our calculations for aluminum, published in 1948, convinced us of the possibility of using the "calculation temperature" to eliminate finite series errors. In our subsequent investigations on electron-density distribution we made no detailed calculations to justify the calculation-temperature method that we used, as we considered that the results obtained for aluminum showed that it gave rise to no doubts. Since doubt has now been expressed concerning the possibility of using this method without distortion of the results on the electron-density distribution, it is necessary to make a more detailed examination of the effect of the calculation temperature. Let us examine the proofs that have been offered of the impossibility of using the calculation temperature without distorting the calculated electron density.

Konobeevsky considers that the calculation temperature may obscure important distribution differences that are the subject of the analysis. In support of his assertion Konobeevsky refers to the work of Kritskaya and Rovinsky [13], which leads to the conclusion that the "calculation temperature" introduces appreciable distortion into the calculated electron-density distribution. This work, however, contains defects, which are so serious that the authors' conclusion can be disregarded.

In the first place, the authors come to the incorrect conclusion that agreement of experimental values of the atomic scattering factor with the theoretical curve, calculated by Hartree's method, forms a criterion of the correctness of the experimental results. Such agreement, although of interest, cannot confirm the reliability and accuracy of results obtained experimentally. It is, therefore, unsound to lengthen the experimental f-curve with the aid of values of the atomic factor calculated theoretically by Hartree's method. No basis can be found for this method, nor is it possible to determine the error introduced by this method of manipulating the experimental results. This half-experimental, half-theoretical curve cannot give a true picture of the electron-density distribution. The theoretical Hartree curve for the atomic factor is obtained from a definite, given electron distribution, and it is obvious that the reverse calculation of electron distribution from this curve must give the original, given picture of the distribution. The invalidity of this method of combining experimental and theoretical curves will be obvious from what we have said. The electron-density distribution obtained from a "mixed" curve of this sort must give a picture that is also mixed; it will not be in accord with our theoretical postulates and cannot be regarded as resulting from experimental data: it is rather a distortion of both.

In their interpretation of their results, Kritskaya and Rovinsky [13] make the assumption that in the copper crystal the atoms are in the univalent condition. On the basis of this unfounded supposition, they make calculations that are inconsistent with their hypotheses and conclude that the picture has been distorted by the temperature factor. The authors, moreover, consider that they have in this way made a quantitative estimate of the distortions, on the basis of which they introduce corrections.

Finally, the authors calculate the electron density to the third place of decimals, which is considerably beyond the possible accuracy of the determination of the f-curve, and on this accuracy the accuracy of the electron-density calculation depends. At present the f-curve can be determined for aluminum accurate within $\pm$ 0.05; for copper the accuracy is still less. The electron density can be determined with the same accuracy. Calculation of the electron density to the third place of decimals cannot, therefore, be justified.

It will be seen from the above that Kritskaya and Rovinsky's results [13] must be accepted with great caution, and their conclusions even more so, although it follows from their results that at a sufficiently large distance from the center of an ion the electron density is independent, within experimental error, of the "calculation temperature". The doubts raised by Konobeevsky [18, 14, 17] have, therefore, little basis, and they are in conflict with the experi-

mental results and the conclusions that may be drawn from them.

We pass to an examination of the arguments advanced by Snow [16] in support of his opinion regarding the inadmissibility of the use of the "calculation temperature". Snow considers that the bridges of increased electron density found by us can be attributed entirely to the method of calculation that we have used. In his opinion the "calculation temperature" increases the electron density at the point half way between neighboring atoms, and, as a result of the summation of overlapping electron-density distributions of spherical atoms, it causes an apparent bridge bond. In support of his point of view Snow makes some simple calculations. He considers the electron-density distribution for spherical atoms disposed at great distances apart in the lattice. He then moves them to the distance corresponding to the disposition of the atoms that are closest together in the lattice and makes a summation of the electron density at individual points, thus obtaining values that agree with those found by us experimentally, which leads him to the conclusion that the bridges are the result of the method of calculation. This sort of proof cannot withstand criticism. Snow, in using such a method of calculation, is asserting — consciously or unconsciously, I do not know — that 1) atoms have spherical symmetry; 2) atoms remain unchanged with respect to electron-density distribution when they enter a crystal lattice; 3) the electron-density distribution of an atom is independent of its position in the lattice; 4) the electron density in a crystal lattice is the result of a simple summation of the electron densities of the separate atoms.

All four assertions are incorrect. Such atoms are unknown to modern science. Modern science teaches us that an atom is variable, and that its state depends on the surrounding conditions (including its position in the lattice), the spherical symmetry of an atom being only a particular case of its form, which depends on the medium. A crystal cannot be regarded as the simple sum of its atoms. It is impossible to treat a separate atom in a crystal and study it apart from the conditions of its existence, just as it is impossible to compound the separate atoms together on the assumption that the simple sum of them comprises the crystal lattice. In actuality, atoms, in forming a crystal lattice, undergo change. They interact, pass into other states, and change their form. The crystal lattice is formed as a result of the conflict between two tendencies: attraction and repulsion between the electron envelopes of atoms. According to the strength and nature of the interacting atoms, one or other characteristic of the chemical bond may be manifested.

2. Let us pass to the question of the interpretation of the observed "bridges" of increased electron density. In order to obtain a correct explanation of the "bridges" of increased electron density it is necessary to establish correct principles from which to start. As already pointed out, it will be correct to regard the crystal as a single whole, and not as the simple sum of its atoms. An atom in a crystal must be treated as being in a state modified by surrounding conditions. The nature of the interaction of atoms is determined by the result of the conflict between two tendencies: attraction and repulsion of electrons.

From the point of view of these principles, the determination of electron density is a good experimental method. In the application of this method it is not necessary to start from any assumptions regarding the form or state of the atoms, or the nature of their interaction. By measurement of the intensity of X-rays scattered by the crystal — and the scattering is actually produced by the electrons of the atoms — we may determine the curve of electron-density distribution for any directions in the crystal. The resulting electron-density curve may be regarded as a curve showing the probability of finding an electron in one or other place in the crystal lattice. This method, therefore, does indeed treat the crystal and the electrons distributed within it as a single whole; it does not separate individual atoms, but gives only the curve showing the probability of finding the electrons of atoms composing the crystal lattice; it gives a topographical picture of the electron-density distribution, and it reveals the places of increased and reduced electron density.

Only in this way is it possible to interpret the picture obtained of the electron-density distribution: it is obtained by a direct experimental method and is a picture of the actual distribution of electrons (or probability of finding an electron) in the crystal lattice; it exists irrespective of any assumptions and hypotheses concerning the form and state of the atoms, etc. Hence, in accordance with modern ideas concerning the chemical bond, the lines of high electron density between the atoms (bridges) correspond to the highest binding force. Treatment of the places of increased electron density as the result of the simple superposition (summation) of electron densities leads to the necessity of treating the atom as unchangeable and spherical, which is contrary to modern scientific ideas.

3. With respect to the possibility of determining the degree of ionization of an atom from a study of electron density, two objections have been made.

Konobeevsky [17] considers that the method by which we calculated the degree of ionization of aluminum atoms is doubtful and arbitrary. The method that we have used is, of course, to some extent conditional in character, but it has quite a sound basis, and, moreover, methods of this sort are often used in all sorts of calculations in crystal-

lography. Thus calculations and operations made with atomic radii are also conditional in nature, but no one would assert that this method is doubtful or arbitrary. The conditional nature of the method arises from the difficulty in the exact separation of the space occupied by ions from that occupied by conductivity electrons. The boundary between ions and conductivity electrons is, of course, a conventional one, as all of our studies on the determination of electron density have shown, but the error introduced into the calculation by the inaccuracy in the determination of this boundary has, according to our calculations, no effect on the final result. It is, of course, impossible to give an absolute significance to the resulting values. It may, however, be asserted that the ionization of an aluminum atom present in a crystal lattice is incomplete.

Snow [16] considers that it is overoptimistic to treat a difference of 0.04 e/A^3 in electron density as significant and make inferences from it. As we have shown in our work, the determination of the electron density of aluminum is accurate within $\pm$ 0.05 e/A^3, so that it is clear that a value of 0.04 e/A^3 lies beyond the limits of the experimental accuracy. The matter, however, is quite different in our calculation, in which we have used not individual determinations of electron density, but the whole curve derived from nine determinations; not one of these stands outside the limits 0.16-0.24 e/A^3, and they give the mean value of 0.20 e/A^3. There is now no reason to doubt this result.

With regard to the fact that the theoretically calculated atomic factor curves for variously ionized aluminum do not differ, Snow does not take into account that the theoretical curves are constructed on the basis of quite definite assumptions and cannot form a verification of the experimental f-curves. With respect to the effect of valency electrons on the f-curves, it may be pointed out that this effect increases as $\sin\theta/\lambda$ falls, and gradually diminishes as the latter quantity rises. According to our results this effect is appreciable up to $\sin\theta/\lambda = 0.44$, i.e., for the reflections 111, 002, 022, 113, 222, and not only for 111, as Snow asserts.

In concluding this section, I must point out that the result obtained for the degree of ionization of the aluminum atom cannot be regarded as quantitative, but only as qualitative. We may, therefore, insist on the accuracy of our assertion concerning the incomplete ionization of the aluminum atom in the crystal. This is how it is expressed in our paper, and it is only in this way that the results obtained can be interpreted.

4. Snow asserts [16] that we have selected unfavorable radiation requiring a large dispersion correction that may mask small differences in intensity. He criticizes our correction, which was calculated theoretically by Hepple's method, and prefers the experimentally determined correction of Brindley and Ridley, forgetting to point out that the corrections that have been experimentally determined by different authors vary so much that there is no possibility of using them.

Konobeevsky and Mamedov's Method of Trial

In his paper "Investigation of the Structure of Atoms in Crystals by the Method of Trial" Konobeevsky [14] states "... it is not very expedient to attempt to find the actual radial electron-density distribution in an atom (both when free, and particularly when present in a crystal) from the direct measurement of the diffraction spectrum, and subsequently bringing it into relation with the atomic space. A more justifiable method is the method of trial, which consists in the theoretical construction of the function $\rho(R)$, the calculation of the diffraction spectrum F(H), and the comparison of this with experiment. This method of trial can be recommended also because, as we shall see below, it permits us to investigate the function $\rho(R)$ "by parts". The distribution in the atom can be expressed at first in a fairly general form by the introduction of some parameters, in the course of which the symmetry conditions must, of course, be applied. When we pass to the function F(H), this will be found to depend on the same parameters, but for the determination of these it is not necessary to know exactly the whole course of the function F(H); it is sufficient to use only a few points and to compare the separate interferences."

It will be seen from this that Konobeevsky considers the method of trial to be the most perfect method for the solutionof the problem of the structure of atoms in crystals. The method of trial, however, has been previously applied fairly frequently for the solution of various problems. Thus, in the determination of crystal structure one assumes the positions of the atoms, calculates the intensities of the X-rays that would be scattered by this structure, and then makes a comparison with the experimental results. But this method of trial is used when there is no direct method. It cannot, in any case, be said to be more perfect. The more perfect methods are the objective, direct methods, such as the recent Fourier series method, which enables us to obtain an objective picture of the distribution and structures of atoms without any preliminary suppositions concerning the nature of this picture. The second advantage that Konobeevsky attributes to the method of trial is also more in the nature of a defect in the method than of one of its merits. In all investigational work, individual measurements are never to be regarded as more trustworthy than the obtaining of a series of functional results. In the second case fortuitous error in the measurement of any quantity can always be readily detected by the nonconformance of the value to the general series of values. When

single measurements are made, this sort of control is absent. The investigation "by parts" of a few points of the individual interferences is a defect in the method of trial.

The results of Konobeevsky and Mamedov's investigation of aluminum [19] are also contrary to the method of trial. According to these results the electrons of an aluminum atom in the crystal tend to move out of the direction (111), and also (110), and into the direction (100), i.e., tend to fill the structurally freest places (octahedral pores) of the face-centered lattice. The "bridges", therefore, are directed not toward the nearest neighbor (110), but along (100). Our knowledge of atomic interaction tells us that interacting atoms approach one another: the stronger the interaction, the shorter the distance, and the greater the electron density between them. According to Konobeevsky and Mamedov's results, the greatest electron density (bridge) occurs in the direction (100), whereas, as is well known, the shortest distance corresponds to the direction (110). Again, the directions (100) and (111) of the aluminum lattice both pass through the octahedral pores, and it is quite incomprehensible how electrons that fill the "structurally freest places" can at the same time move from the direction (111) into the direction (100).

Conclusion

In conclusion it must be pointed out that the method of determining electron density for the solution of the question of the nature of the chemical bond is one of the direct methods for the investigation of this problem. It is deserving of great attention from investigators whose work is directed to the study of the nature of the chemical bond.

The views recently expressed abroad (Snow) and here (Konobeevsky, Boky) with respect to the defects of the electron-density method are erroneous and are in conflict with the experimental data and the inferences that can be drawn from them.

Note. I have not discussed Boky's views because his utterances comprise only a few words expressing doubts concerning the electron-density method, without providing any basis for his opinion.

Received April 27, 1953

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* See Consultants Bureau Translation, page 31.

CURRENT EVENTS

ELECTION OF ACADEMICIANS AND CORRESPONDING MEMBERS* AT THE ACADEMY OF SCIENCES OF THE USSR

At a session of the Division of Chemical Sciences of the Academy of Sciences of the USSR held on October 19 and 20, 1953, candidates were selected for election as academicians and corresponding members of the Academy.

At a general meeting of the Academy of Sciences of the USSR held on October 23, 1953, the following were elected by secret ballot as academicians in chemistry: B. A. Arbuzov, V. A. Kargin, V. N. Kondratyev, I. L. Knunyants, and I. N. Nazarov; and the election by the Division of the following corresponding members was confirmed: O. A. Alekin, I. P. Alimarin, K. A. Andrianov, Ya. I. Gerasimov, N. M. Zhavoronkov, M. I. Kabachnik, V. V. Korshak, D. N. Kursanov, P. A. Moshkin, B. P. Nikolsky, A. V. Novoselova, I. V. Petryanov-Sokolov, N. K. Pshenitsyn, A. P. Terentyev, K. V. Chmutov, G.I. Chufarov, M. M. Shemyakin, and N. I. Shuikin.

There were 98 candidates for 23 vacancies as academicians and corresponding members in chemistry. Most of the candidates were registered under special subjects (28 candidates under physical chemistry and 21 candidates under chemical technology). In the preparatory work before the elections it became clear that the academician members of the Division had a difficult task ahead of them: to select the most worthy from a large number of candidates.

New Academicians: Special Subject "Organic Chemistry"

Boris Aleksandrovich Arbuzov is one of our greatest organic chemists, a worthy representative and continuator of the remarkable tradition of the Kazan school of chemists, which is so successfully developing and extending the ideas of A. M. Butlerov. In his 25 years of scientific activity B. A. Arbuzov has worked in a number of fields of organic chemistry, of which three must be given special mention: the chemistry of the terpenes, the chemistry of diene compounds, and the chemistry and structure of organophosphorous and other organometalloid compounds. While making a study of turpentine and derived substances in 1930, B. A. Arbuzov carried out extensive investigations on the chemical reactions of terpenes, which led, after many years of persistent work, to important generalizations and discoveries. His investigations on the isomerization of bicyclic terpenes into terpenes having an open linkage, subsequently known as the B. A. Arbuzov rearrangement, were of outstanding theoretical and practical significance.

B. A. Arbuzov succeeded in establishing the structure of levopimaric acid, a substance of considerable practical importance, and in so doing he solved a problem upon which some of the greatest chemists of the world had worked for more than 100 years. By brilliant application of the diene synthesis to the proof of the structures of alloocimene and levopimaric acid, B. A. Arbuzov made new and valuable contributions to the understanding of the actual mechanism of the diene synthesis on the basis of modern electronic concepts. With the aid of the diene synthesis he has prepared a large number of new compounds having practical importance in perfumery and in the dye industry (for the preparation of heterocyclic compounds derived from selenophene and thiophene).

The second, and main, direction of B. A. Arbuzov's investigations is the study of the properties, structures, and methods of synthesis of organophosphorus and other organometalloid compounds.

Applying Academician A. E. Arbuzov's classical method for the preparation of phosphonic acids, B. A. Arbuzov synthesized a number of new types of phosphonic acids, containing various heterocyclic rings, thus demonstrating the generality of this method and the possibility of its application to the most varied types of halogen-containing organic compounds.

Valuable results have been obtained by B. A. Arbuzov by application of the parachor method to the study of the structures of esters of phosphoric, phosphorus, phosphonic, dialkylphosphorus, formic, orthocarbonic, and orthosilicic acids, and also of cyclic organic compounds, to which he was the first to apply the parachor method for the determination of fine structure. B. A. Arbuzov obtained material of no less interest and importance by the study

* Photographs of the new Academicians and Corresponding Members which accompany this article in the original Russian journal have not been reproduced in this translation because of limitations imposed by our reproduction process. Publisher.

of organophosphorus and other types of compounds with the aid of dipole moment measurements, which enabled him to draw a number of inferences with respect to their structure and, in particular, with respect to the disposition of allyl groups in space and the possibility of the free rotation of individual groups and parts of the molecules.

Ivan Lyudvigovich Knunyants is one of the highest authorities on the chemistry of heterocyclic compounds; of particular importance are his studies of pyridine derivatives, in the course of which he worked out a number of elegant syntheses (pyridine analogs of Michler's ketone and hydrol, dyes of the triphenylmethane type, etc.). In his work on the synthesis of carbocyanine dyes, which has found practical application, he has made valuable contributions to the chemistry of coloring matters. He has done very important work on an original method for the synthesis of 5-hydroxy-2-pentanone, required in the manufacture of quinacrine and pamaquine. The results of this investigation are already being applied in industry. Knunyants' work on the splitting of epoxides resulted in a number of achievements, including the synthesis of 2-fluoroethanol, which made the syntheses of numerous organic fluorine compounds possible. A similar scission reaction with ethylene sulfide provided material for the synthesis of 2-aminoethanethiols, which are starting substances for the preparation of analogs of certain antibiotics. Somewhat apart from these stand his investigations on the structure of the antimalarial preparations plasmocid, pamaquine, and quinacrine, and the subsequent devising of methods for the preparation of these compounds; particularly important is his so-called "chain" for the synthesis of pamaquine and quinacrine. There can be no doubt that I. L. Knunyants is a very high authority in this field.

In 1946 I. L. Knunyants was elected a corresponding member of the Academy of Sciences of the USSR. In the short time that has elapsed since then he has published more than 25 original papers. Very important investigations described in these include studies relating to the introduction of fluorine into organic compounds, syntheses of hydroxyalkylphosphines, the Beckmann transformation of such complex oximes as those of ionone, the tetralones, and cyclic ketones in general, and studies also of 6-caprolactam, the polymerization of fluoro olefins and unstable cyclic compounds, and the preparation of other macromolecular compounds. His investigations on the addition of hydrogen sulfide and thiols to olefins are very important: the results of these researches have great significance for the synthesis of many physiologically and pharmacologically active substances. Apart from theoretical investigations, I. L. Knunyants has devoted much attention to the study of theoretical organic chemistry, particularly to questions of structural theory.

The third organic chemist to be elected was Ivan Nikolaevich Nazarov, whose scientific activities over the period 1933-1953 have developed in the following directions.

The first group of Nazarov's researches was devoted to the study of free radicals of the aliphatic and aliphatic-aromatic series, namely, the so-called metal ketyls obtained by the action of sodium on branched ketones such as hexamethylacetone and trimethylacetophenone. As a result of these investigations, which revealed the possibility of the existence of stable radicals containing tervalent carbon, a number of studies appeared on the isomerization of olefinic hydrocarbons containing tertiary radicals, which occurs owing to their elimination at comparatively low temperatures.

The second large group of investigations was devoted to the chemistry of acetylene and 1-butene-3-yne. Above all, we must refer to the studies of vinylethynylcarbinols, the simplest member of which is manufactured on the large scale by Nazarov's method and is used for the preparation of new adhesives (Nazarov's "Carbinol Glue"). Vinylethynylcarbinols have served as a basis for the opening of a new field in the chemistry of unsaturated compounds. Among very important applications of 1-buten-3-yne in the preparation of new compounds we may cite the synthesis of vinylisocoumarins and divinyl ketones, and the cyclization of dienones to give substituted cyclopentenones. The last reaction has been particularly fruitful, since it has made possible the ready preparation of a variety of mono- and poly-cyclic compounds having a five-membered ring.

The third group of Nazarov's researches was devoted to the synthesis of heterocyclic compounds containing a piperidine, pyran, thiopyran, or furan ring from divinyl ketones and allyl vinyl ketones. Some of these were found to be physiologically active, and further work led to the synthesis of a new sedative, promedol, which is more active than morphine and has no toxic properties. Promedol is now prepared on the large scale as a medicinal.

The fourth group of Nazarov's researches was devoted to the synthesis of polycyclic compounds by the use of 1-buten-3-yne; these included compounds related to steroids. He effected the total synthesis of a number of compounds of the cis-cis series having the ring systems of androstane, homoandrostane, estrane, and their heterocyclic analogs. By this means the way has been made clear for the solution of one of the main problems of modern organic chemistry – the chemistry of steroids. Nazarov's work in this direction made it necessary to undertake a number of theoretical investigations relating to the mechanism of the diene synthesis and its stereochemistry. Taken as a whole, Nazarov's work, owing to its purposeful character and its wide scope, is a very great contribution to contemporary

organic chemistry, and it allows us to consider the author to be one of the greatest living organic chemists.

Special Subject "Physical Chemistry"

Valentin Alekseevich Kargin, now elected academician, is a great physical chemist. He is the author of more than 120 papers on various questions in physical and colloid chemistry. In the early years of his scientific activity he made an extensive investigation of colloidal systems, which led to a fundamental change in our concepts relating to the nature and stability of solutions of hydrophobic colloids. In his studies, Kargin showed for the first time the way in which chemical phenomena play a determining role in the formation and in the stability of solutions of hydrophobic colloids.—a consequence of chemical change in the surface layer of the colloidal particle during reactions with substances dissolved in the intermicellar liquid. These concepts were subsequently successfully applied by Kargin in the study of ion exchange in soils, in the development of a method for strengthening water-saturated sandy foundations, and in the discovery of a new method for the purification of colloidal solutions and precipitates from electrolytes with the aid of electrodialysis. These two methods are used in large-scale practice.

During recent years Kargin's investigations have been mainly directed to the study of the structure and properties of macromolecular compounds, such as cellulose, plastics, rubbers, and proteins. By his investigations of solutions of high polymers V. A. Kargin has shown that they must be regarded as systems in thermodyanamic equilibrium, and that the dissolution of amorphous polymers should be regarded as a process equivalent to the mixing of liquids.

By means of structural investigations, in which electronographic and X-ray methods are used in conjunction, Kargin has established that cellulose and a number of its derivatives are, in spite of the views of foreign investigators, to be regarded as amorphous. Kargin and his coworkers have carried out extensive investigations on the mechanical and thermodynamic properties of polymers; they have studied relaxation processes occurring in the deformation of polymers, developed methods for estimating the flexibility of polymer molecules, elucidated the mechanism of the deformation of crystalline polymers, and performed a number of other investigations relating to physical chemistry and polymers.

In recent years Kargin has undertaken the task of constructing a theory that will permit us to synthesize polymers of predetermined properties, and he has already obtained a number of important results. Kargin has developed the thermomechanical method of investigation, established the existence of three states in amorphous-liquid polymers (glassy, highly elastic, and plastic flow), discovered the relation between the form of the deformation-temperature curve and the structure of the polymer and its molecular weight, given a quantitative method for estimating the flexibility of polymers from their thermodynamic and mechanical properties, established the peculiarities in the structure of polymer crystals (defects), and studied the mechanism of deformation and shown that deformation is accompanied by a peculiar type of recrystallization. The theory developed by Kargin is used in practice in the synthesis of new polymers having special properties.

Another academician in physical chemistry is Viktor Nikolaevich Kondratyev, an eminent worker on chemical kinetics, the structure of substances, molecular spectroscopy, photochemistry, and other branches of physics and physical chemistry. His principal investigations concern elementary chemical processes and the mechanism of complex chemical changes. Kondratyev is one of the founders of the modern electronic theory of molecules. In this connection particular mention may be made of his investigations on the dissociation of nitrogen, bromine, and salt vapors under the action of electrons and light quanta, and also of his studies of molecular heats of dissociation, and the mechanism of the formation of molecules from free atoms and radicals. In particular, Kondratyev was the first to determine correctly the heat of dissociation of molecular oxygen. It should be noted that already in 1924 Kondratyev applied for the first time the method of mass-spectroscopic analysis in the determination of the dissociation products obtained from salt vapors when bombarded with electrons.

These first researches of the period 1924-1934 already marked Kondratyev as one of those developing the application of modern physics to chemical problems. Kondratyev's further work was characterized to an even greater extent by its leaning toward chemistry. The main line of these investigations was the study of the properties of free radicals and the elucidation of their role in chemical kinetics.

V. N. Kondratyev was the author of a very effective spectroscopic method (line-spectrum absorption method) for the identification and quantitative determination of free radicals. With this method he studied various properties of free hydroxyl and detected the appearance of this radical in many combustion reactions; he also elucidated the important part played by hydroxyl in these reactions. Kondratyev showed that other free radicals, apart from hydroxyl, were formed in many oxidation reactions, for example SO and CS radicals, and he made quantitative studies of their formation and disappearance.

Kondratyev's further investigations led him to infer the presence of large concentrations of atomic hydrogen in the rarefied zone of the hydrogen flame To confirm this inference he developed a special method for the determination of free atoms during the course of chemical reactions, in which the heating effect occurring at a surface catalyzing the recombination of atoms was utilized. The results obtained by this method fully confirmed the deductions made from the theory. Taken as a whole Kondratyev's researches form the first kinetic investigation in which a systematic study of the separate intermediate substances and their reactions has led to the derivation on a sound basis of the mechanism of a complex reaction and its substantiation by experiment. These studies indicate the direction that must be taken by investigations into the mechanisms of other complex reactions.

New Corresponding Members: Special Subject "Organic Chemistry"

Martin Izrailevich Kabachnik is a specialist on organometallic and organometalloid compounds, on heterocyclic compounds, and on theoretical organic chemistry. Although essentially a worker in synthetic organic chemistry, M. I. Kabachnik has systematically directed his investigations also to the solution of practical questions in the neighboring fields of physiology, biochemistry, medicine, and agricultural science. The greater part of his investigations and inventions are concerned with organic synthesis; he has discovered new chemical reactions and developed new synthetic methods on their basis. For example, he has proposed a method of synthesizing β-halogenated esters of phosphorus acid, 2-haloalkylphosphonic acids and various of their derivatives, and esters of vinylphosphonic acid. These methods are based on the reaction of alkylene oxides with halogen compounds of tervalent phosphorus, which has been studied by Kabachnik. He is to be attributed also with the method of synthesizing 1-haloalkylphosphonic acids on the basis of a new reaction between aldehydes or ketones and halogen compounds of tervalent phosphorus. Recently Kabachnik has developed a method for the synthesis of α-amino phosphonic esters from aldehydes, dialkyl hydrogen phosphites, and ammonia, on the basis of a reaction that he has discovered.

Apart from the development of new synthetic methods, one of the main objects of Kabachnik's investigations has been the discovery of new classes of organic compounds, by the use of which the solution of particular theoretical or practical problems may be possible He has synthesized the first members of new classes of compounds, such as α-keto phosphonic esters, vinylphosphonic acids, β-halogenated esters of the acids derived from tervalent phosphorus, 2-haloalkyl phosphonic acids and their esters and other derivatives, α-amino phosphonic acids (phosphorus analogs of the biologically important amino acids), dialkyl hydrogen phosphorothioites, derivatives of aminoanabasine, and pyracridones A number of Kabachnik's investigations are devoted to the solution of theoretical problems of organic chemistry. There are, for example, his studies of the mechanisms of some organic reactions: the amidation of heterocyclic compounds ofthe pyridine type by means of alkali-metal amides, the isomerization of 2-haloalkyl phosphites by heat, and the reaction of aldehydes with phosphorus trichloride.

The most important of Kabachnik's theoretical investigations are those relating to tautomerism. He was the first to develop a quantitative theory of tautomeric equilibrium and to make an important generalization concerning the reactivities of tautomeric and nontautomeric substances of dual reactivity. On the basis of new theoretical concepts on tautomerism, Kabachnik has carried out a series of experimental investigations, both synthetic and physicochemical, in which he has found confirmation of the concepts that he has developed.

Aleksandr Petrovich Terentyev is the author of well known investigations on the synthesis of heterocyclic compounds of the pyrrole and indole series, which he began in the early days of his scientific activity. A. P. Terentyev is a pioneer in the application of the Grignard method. He has succeeded in applying the sulfonation reaction, previously largely confined to aromatic compounds, to the main types of five-membered heterocycles (furan, pyrrole, indole). He has since developed the method of sulfonating acidophobic compounds, and in this way new classes have become available: sulfonic acids derived from diene hydrocarbons, quinones, furan derivatives, pyrrole, indole, etc. Terentyev and his coworkers have carried out a whole series of investigations on the chemistry of acrylonitrile and dienes, beginning with a study of their polymerization, and finishing with various syntheses.

A. P. Terentyev has carried out important investigations in stereochemistry. Here we must particularly mention the study of the syn-anti isomerism of oximes of heterocyclic ketones. Of special interest are his recent papers on absolute asymmetric synthesis, which have great methodological importance. For a number of years Terentyev has worked on organometallic and complex compounds, and has also discovered and developed a method for the condensation of alcohols inpresence of magnesium. A number of internal-complex compounds of novel structure have been applied by Terentyev as organic analytical reagents for metals.

Mikhail Mikhailovich Shemyakin has a great mastery of theory and experiment in organic chemistry. In recent times he has become the leading Soviet specialist in the chemistry of antibiotics. M. M. Shemyakin's book, "The Chemistry of Antibiotics", already in its second edition, is well known as are the syntheses that he has introduced for synthomycin and levomycetin, the best remedies for typhus, trachoma, and dysentery. Shemyakin has

published a large number of original investigations on various questions of organic chemistry. His theory of the hydrolytic scission of the C—C bond is very important: it has revealed the source, nature, and mechanism of many widely found types of chemical reactions. It may be emphasized that on the basis of this theory Shemyakin has succeeded in elucidating many important ttansformations of the antibiotics actidone, humulone, streptomycin, and others. In this series the explanation of the formation of maltol from streptomycin is particularly interesting, since it indicates the way in which a straight-chain carbohydrate can be converted into a branched-chain carbohydrate. Shemyakin has succeeded in explaining from the point of view of this theory the essential features of the transamination and α-decarboxylation of amino acids, the β-decarboxylation of amino dicarboxylic acids, and the breakdown of γ-keto α-amino acids and many other reactions of a biochemical nature.

Among other theoretical studies by M. M. Shemyakin, mention may be made of his investigations into the chemistry of aldehydic acids, which completely cleared up the question of the structure of these compounds and made it possible for him to find a general method for the conversion of aldehydic acids into compounds of the quinoline and isoquinoline series. Related to these studies are his investigations on the thermal decomposition of salts, in the first place salts of aldehydic acids, and later of carboxylic acids in general. Shemyakin's investigations on other carbonyl compounds are of importance, particularly those on quinones, which have now led to the development of a general method for passing from a quinone and its derivatives to diketo, hydroxydiketo, and triketo carboxylic acids of the alicyclic and aromatic series.

Shemyakin's investigations on sulfamide preparations (preparation of soluble sulfamides, etc.) are of great practical interest. His studies of the chemistry of vitamins are also very valuable. Shemyakin has made a particularly careful study of the tautomeric transformations in the vitamin B_6 group, and has explained the significance of codecarboxylase in amino acid exchange.

Nikolai Ivanovich Shuikin, a student of N. D. Zelinsky, has worked on the catalytic transformations of hydrocarbons and other organic compounds. Apart from his original theoretical investigations on the dehydrogenational catalysis of hydrocarbons, N. I. Shuikin has carried out a number of important investigations relating to the preparation of individual aromatic hydrocarbons of great economic importance from petroleum. In the same field he has made extensive investigations directed to the detailed study of a complex of questions relating to the problem of the refining of motor fuel by contact-catalysis reactions. Shuikin has developed methods for the preparation of high-quality aviation spirit from the usual straight gasolines and a valuable motor fuel from low-quality sulfurous gasolines.

Shuikin's second important line of work concerns hydrogenational catalysis in the furan series, which has led to a new method for the synthesis of tetrahydrofuransin presence of palladium and nickel catalysts.

Shuikin's third line of work is concerned with the catalytic dehydration of organic compounds, namely alcohols and mixtures of alcohols with amines or ammonia. He has developed methods for the catalytic synthesis of monoalkylanilines.

Special Subject "Organic Chemistry and the Chemistry of Labeled Atoms"

The scientific work of the new corresponding member Dmitry Nikolaevich Kursanov has been concerned with reaction mechanisms and the relation between chemical structure and reactivity in organic compounds. In recent years D. N. Kursanov has extensively and successfully applied the method of labeled atoms in the investigation of these problems.

Kursanov's work on the dehydration of alcohols has thrown light on the course of these important reactions. It has been established that they proceed by a heterolytic mechanism, in which the first, determining step of the reaction is the splitting of a hydroxyl group from the alcohol. In this connection the general nature of dehydrating agents has been elucidated, and the mechanism of possible side processes has been determined.

His second group of investigations include the study of a large number of reactions occurring in presence of aluminum chloride: the Fries rearrangement, the condensation of esters with aromatic compounds (which was discovered by Kursanov), the rearrangement of arylamides, and the new reaction, discovered by Kursanov, of ethyl formate, and also the ethyl esters of some other acids, with benzene, resulting in the formation of 9,10-dimethylanthracene.

A third group of investigations is devoted to a study of quaternary ammonium compounds. Kursanov has discovered a series of new reactions and has determined their mechanisms. According to Kursanov's results, at the basis of the reactions of quaternary ammonium compounds lies their tendency to undergo heterolytic breakdown with formation of a carbonium ion, the electron-accepting properties of which act as the motive power in many alkylation and radical-exchange reactions, etc. These three groups of investigations are unified by the general object of dis-

covering the mechanism of heterolytic organic reactions, the part played by electron-acceptor particles, and methods for their formation or activation. Kursanov has studied the comparative mobilities of hydrogen atoms in 2,4-pentanedione and its aluminum and cobalt derivatives, and also the comparative mobilities of hydrogen atoms in various cyclic and bicyclic ketones. It has been shown that the mobilities of these hydrogen atoms depend greatly on the structures of the ketones and, in particular, on the dispositions of the carbonyl groups and the character of their conjugation with the C—H bonds of neighboring carbons.

Another line of Kursanov's investigations, also carried out with the aid of labeled atoms, is concerned with reaction mechanisms in organic chemistry. In a study of polycondensation reactions it was proved directly that these technically important reactions are accompanied by transesterification at the expense of ester linkages. A study of the mechanism of the cyclization of dienes formed by the hydration of vinylacetylenes in presence of deuterophosphoric acid gave proof of the ionic nature of these reactions, and the determination of the position of the deuterium in the molecule of the resulting cyclic ketone led to important conclusions concerning the structure of the dienes entering the cyclization reaction.

A new and most brilliant discovery by D. N. Kursanov in the field of isotopic hydrogen exchange reactions is that saturated hydrocarbons containing a tertiary carbon atom are able to exchange all of their hydrogen atoms for deuterium in the presence of deuterosulfuric acid, whereas hydrocarbons that contain no tertiary branching are quite unable to undergo hydrogen exchange. On the basis of his experimental results Kursanov has concluded that the hydrogen-exchange reaction in saturated hydrocarbons has a chain mechanism.

Special Subject "General and Inorganic Chemistry"

The work of the new corresponding member, Aleksandra Vasilyevna Novoselova, has been mainly concentrated on the chemistry of rare elements. A. V. Novoselova has carried out extensive investigations on beryllium. She has studied the interaction at high temperatures of silicon tetrafluoride and sodium fluosilicate with beryllium oxide. The application of thermal analysis to the system formed by sodium and beryllium fluorides, and also an X-ray investigation of the phases formed, enabled Novoselova to establish the existence of the previously unknown compound of composition $NaF \cdot 2BeF_2$, of polymorphic modifications in sodium fluoberyllate and beryllium fluoride, and of a new hexagonal crystalline modification of anhydrous beryllium fluoride. Novoselova has made a large number of studies of aqueous systems containing beryllium fluoride and fluorides of other metals, i.e., ternary systems. In practically all of these systems new, previously undescribed compounds were discovered The results of these studies have helped in the explanation of leaching processes. Apart from the fluoride and its derivatives, she has studied other beryllium salts, in particular, the sulfates. For this purpose two ternary, one quaternary, and one five-component aqueous-salt system formed with sulfates of other metals were studied. Very valuable material was obtained in these experiments, enabling the characterization of a series of new double sulfates. She has also studied systems characterizing the cosolubilities of beryllium chloride with other chlorides in water The results obtained have considerably extended our information on the complex and double compounds of beryllium. She has carried out a series of investigations on the tensimetric study of beryllium sulfates and nitrates.

For the second vacancy in this special subject, Nikolai Konstantinovich Pshenitsyn was elected. This worker has applied his knowledge to the development of an extremely complex and difficult subject: analysis of the platinum metals. He has carried out an investigation into the rearrangement (isomerization) of complex compounds of platinum, and at the same time he has studied the chemistry of iridium, obtaining a series of compounds that can characterize this element, namely chloronitrites and sulfito salts having extremely characteristic properties. N. K. Pshenitsyn has investigated the hydrolysis of platinum-metal compounds and of compounds formed by platinum metals with oximes. In both of these investigations it is characteristic that the analytical and purely chemical (inorganic) sides are of equal interest, for the hydrolysis process and the behavior of the oximes are found to characterize the individuality of the platinum metals.

Special Subject "Physical Chemistry"

The new corresponding member Yakov Ivanovich Gerasimov is an eminent investigator on the thermodynamics of metallurgical systems. Ya. I. Gerasimov began his scientific work with an investigation of solubility relations in complicated salt systems and heterogeneous equilibria at high temperature. The general aim of the extensive researches of Gerasimov in this field has been the laying of a foundation for the understanding and calculation of pyrometallurgical changes, and the obtaining of their exact thermodynamic characteristics (free energies of formation). He has carried out numerous investigations of the equilibria between hydrogen or carbon monoxide and the sulfides of zinc, lead, copper, nickel, tin, bismuth, and vanadium. He has worked on the problem of liquid and solid solutions at high temperatures and on methods for calculating the activities of the components in binary and ternary solutions in a number of important systems.

In recent years Ya. I. Gerasimov has studied the thermodynamics of the oxides of nonferrous and rare metals, making a comparison of thermodynamic and crystallographic properties. These investigations include work on the equilibria of magnesium, calcium, and manganese tungstates, and of calcium molybdate, with hydrogen. Gerasimov has carried out extensive investigations on the thermodynamics of equilibrium at high temperatures for systems that are extremely important at the present time. He has also made a number of studies in a wide varity of branches of thermodynamics: thus, he has worked on the surface tension of solutions, activities in electrolyte mixtures, and the use of spectroscopic data in thermodynamic calculations.

Igor Vasilyevich Petryanov-Sokolov is well known as a specialist on the physical chemistry of aerodisperse systems. He has invented new precise methods for the quantitative investigation of aerosols, which permit the determination of the size-distribution of the particles and the distribution of electrical charges on the aerosol particles. These methods, which have received general recognition and wide application, have enabled Petryanov-Sokolov and his coworkers to solve some very important questions relating to the electrical properties of aerosols: to elucidate the mechanism of the formation of charges and the laws of their distribution on the particles of the aerosol, to determine the kinetics of the discharge of aerosols in an ionized atmosphere, and to greatly clarify the question of the stability of charged aerosols.

Petryanov-Sokolov devoted an extensive series of investigations to the mechanism of the formation of charges on aerosol particles obtained by the dispersion of liquids. These investigations developed into an independent branch of the science of aerosols, devoted to the electrical properties of aerodisperse systems.

Petryanov-Sokolov obtained extremely important results in his studies of general questions relating to the stability of aerosols and the mechanism of the formation of aerodisperse systems by means of condensation. A whole series of Petryanov-Sokolov's researches was devoted to questions of the precipitation and trapping of aerodisperse systems. Some of the methods that he has developed to counter the action of aerosols have considerable practical significance.

Konstantin Vasilyevich Chmutov is a worker on surface phenomena whose extensive investigations cover gas and vapor sorption at solid adsorbents, the adsorption of dissolved substances, the kinetics and dynamics of sorption, diffusion phenomena, and questions of adsorptional and ion-exchange chromatography. Chmutov's investigations are original in their conception and their execution. He is widely known as a master of delicate physicochemical experimentation.

In an early series of investigations, carried out by Chmutov in conjunction with his teacher, Prof. N. A. Shilov, an original concept was developed concerning the adsorption of electrolytes, regarded as an ion-exchange process with the products of the activated adsorption, or chemisorption, of oxygen (surface carbon oxides). Later, Chmutov showed in some careful investigations that in a number of cases inversion of absorptional sequencies may occur in the adsorption of organic acids or alcohols on finely porous active charcoals as a result of purely spatial obstacles, increasing in magnitude with increase in the length of the carbon chain. The false equilibria that arise in such systems, and may last for decades, can be broken down by disturbing agents, such as ultrasonic fields. The concepts developed by Chmutov relating to the dynamics of catalytic processes in the nonpoisoned and poisoned layers of catalysts were the first theoretical descriptions of these complicated cases of absorption that were based on exact experiment. Great scientific interest is presented by Chmutov's investigations of capillary-condensation processes in artificial capillary systems; they are the most satisfactory of a number of investigations of this sort. The theoretical analysis of the results of numerous experiments on various vapors led to important conclusions concerning the interpretation of experimental results on the capillary condensation of vapors in porous systems. Chmutov devoted much attention to the study of diffusion processes. Among these investigations, his careful study of the temperature dependence of the diffusion of polymers dissolved in monomers is of fundamental importance, and so also is his work on the diffusion and cataphoretic acceleration of the transfer of dyes in gelatin layers, which is associated with the solution of problems of color photography. Among his recent work on kinetics we may mention the quite original investigations on the mechanism of the growth of colloid particles, in which an electron-microscope technique was used in conjunction with a quite new method of "labeled particles", which permitted the mechanism of the coagulation process to be established. The development of the labeled-particle method resulted in an equally original "surface-development" method, which is of general importance for establishing anisotropy in the surface of various colloidal objects.

The scientific interests of Grigory Ivanovich Chufarov are centered around the study of metallurgical processes. All of his theoretical and practical studies relate to the same field: the kinetics and catalysis of chemical reactions and metallurgical processes. Chufarov has carried out and published a series of investigations relating to the hydrolysis of magnesium chloride and the protection of metals from corrosion by salt solutions. His researches were

carried out in close association with industrial organizations, and they rendered vital assistance in the creation of the Soviet potash-magnesia industry. For a number of years Chufarov was occupied with a study of the process of etching of metals and the theory of the action of retardants for this process. His theoretical researches on the etching of metals and on the retarding action of additives were closely associated with the practical requirements of a number of branches of industry. Special mention must be made of the detailed investigation of the phenomenon, which he was the first to observe, of the retardation of the dissolution of iron-silicon alloys in sulfuric acid containing halide ions, which results from the formation of a surface protective film of lower silicon oxides on the metal. Chufarov has also carried out investigations concerned with the etching of metals and the wetting of their surfaces for application in such operations as the galvanizing and tin-plating of iron and the cold drawing of tubing. A very important line of his work is concerned with the kinetics of the reduction and dissociation of metal oxides. In these investigations Chufarov is developing the original studies of Academician A. A. Baikov in a creative manner. Chufarov and his school have developed an absorptional-catalysis theory of the reduction of metal oxides. His work on the reduction of metal oxides is widely applied in scientific institutes and manufacturing organizations.

Special Subject "Hydrochemistry"

The numerous and important investigations of the new corresponding member Oleg Aleksandrovich Alekin have been entirely devoted to hydrochemistry. The first investigations of Alekin were concerned with a comprehensive hydrochemical study of the Terlets mountain lake, and other lakes of this district of the Altai mountain system and their feeders; he later studied the lakes of the Katum ridge. These studies formed the beginning of his systematic investigation of the lakes, and later the rivers, of the USSR. As a result of these extensive investigations, the three-volume monograph "The Hydrochemistry of the Rivers of the USSR" was published. His direct study of the hydrochemistry of rivers and his thorough acquaintance with all previous material on this subject enabled Alekin to solve a number of methodological and theoretical problems in hydrochemistry. Among his experimental hydrochemical investigations are many concerned with the determination of dissolved oxygen, hardness, oxidizability, pH, and gold, etc., in water; he has set up a number of hydrochemical field laboratories and stations. On the basis of his practical experience he has written "Guide to the Chemical Analysis of Inland Waters" and other hydrochemical handbooks of high merit.

Special Subject "Chemical Technology"

Kuzma Andrianovich Andrianov has worked on the synthesis and technology of macromolecular compounds and dielectrics. In 1937 he began to publish investigations on organosilicon compounds, and these resulted in a wide development of the chemistry of these substances. In 1938 his first papers on the mechanism of the hydrolysis and condensation of alkyltriethoxysilanes appeared: in these he first demonstrated the formation of siloxane bonds in the course of the hydrolysis, leading to the formation of macromolecular organosilicon compounds, the polyorganosiloxanes. Andrianov showed that the size of the saturated organic radical had no effect on the chemistry of the condensation process, but was of importance for the rate and degree of hydrolysis of the ethoxyl groups. When an unsaturated radical was present, however, not only the condensation reaction, but also polymerization occurred, owing to the presence of the double bond. These investigations were continued in studies of the polymeric products derived from trichlorophenylsilane and dichlorodiphenylsilane. These various investigations form the basis of the resins, lacquers, and insulation materials developed by Andrianov. In the treatise "Macromolecular Organosilicon Compounds", which appeared in 1949, Andrianov examines methods of synthesizing monomers, questions relating to the reactions yielding polyorganosiloxanes of different types, and the physicochemical, mechanical, and dielectric properties of various polysiloxanes. In 1951 he published papers on the chemistry of polysiloxanes, in which he proposed a condensational-polymerization mechanism for their formation. Andrianov has carried out much work on the chlorination of biphenyl. The most important result of this work was the isolation of a special type of polychlorobiphenyls, a mixture of which had little tendency to crystallize. These investigations formed the basis for the development of a new liquid dielectric, Sovol. In 1932-1935 Andrianov published a series of investigations on macromolecular compounds in which he studied the kinetics of the condensation of phenols with acrolein and other aldehydes in presence of acid and alkaline catalysts.

In his work on the preparation of soluble resins, Andrianov synthesized hexylphenol-formaldehyde (oil-soluble) and aniline-formaldehyde resins. Of exceptional importance is his work on the formation of polyvinylacetal resins and its use as cable insulation ("Vinflex"). His investigations on electrical insulation are well known, they are given both in papers and in separate monographs. In a series of papers he examines general theoretical questions relating to insulators: stability to heat, chemical reagents, and moisture; inflammability, dielectric properties; etc. In these he makes definite inferences concerning the future course of work with the object of obtaining

the most perfect insulators. The new insulating materials developed by, or under the supervision of, K. A. Andrianov are now applied on a large scale in the electrical industry.

Nikolai Mikhailovich Zhavoronkov is a specialist in chemical technology. His main researches have been devoted to the investigation of processes for the preparation of hydrogen and the purification of gases in the production of synthetic ammonia, and to processes for the separation of liquid mixtures by adsorption, rectification, molecular distillation, and chemical exchange. His investigation on the purification of converter gas from carbon monoxide by means of ammoniacal cuprous salts has found practical application in existing works and in new projects.

Zhavoronkov's work on the solubility and absorption of carbon dioxide by water is also applied in industry, and it is of theoretical importance. A series of Zhavoronkov's investigations is devoted to the study, by means of aerohydrodynamics, of the scrubber process, which is one of the very important questions relating to the construction of absorption, rectification, and other chemical apparatus for effecting separations. In spite of the long and extensive application of scrubbers in industry, the scrubbing process, and in particular the aerohydrodynamic conditions under which scrubbers work, have received little study until recently. This gap in our knowledge has been to a great extent filled by the work of Zhavoronkov, who was the first investigator in the USSR to make a general systematic study of the aerohydrodynamics of the scrubber process. His researches have established the general laws relating to the movement of gas in dry and sprinkled scrubber fillings and to the hydraulic resistance of scrubber fillings and finely ground granular materials, thus enabling the productivity reserves of these and catalyst vessels to be determined and an indication of methods of increasing productivity to be found. Zhavoronkov has carried out an extensive investigation in order to establish the physicochemical regularities to be observed in the separation of mixtures by means of molecular distillation. He has developed methods and apparatus for the separation of mixtures by the method of high-vacuum rectification. He has devised an original, highly efficient horizontal apparatus for absorption, rectification and chemical-exchange processes.

Panteleimon Afanasyevich Moshkin is an expert in industrial organic chemistry. His first technological project, the manufacture of iodine from seaweed, was based on his own experiments on the Murmansk coast.

P. A. Moshkin has devised an interesting synthesis of pyridine compounds by the condensation of aliphatic aldehydes with ammonia; this synthesis is still of importance and is used for preparative purposes. His investigations on the oxidation of paraffins to carboxylic acids are of great importance. In the course of these researches other important work was done, such as the preparation of chemically pure palmitic acid, and the study of the operating conditions required for catalysts used in the fat industry. Moshkin's investigations on the separation of phenols from the resin obtained in the semicoking of coal are of great importance. He worked out technical methods for the preparation of polyhydroxybenzenes, catechol, resorcinol, and xylenols. Moshkin developed a method for the preparation of butanediol and a large number of other substances (about 50) from furfural. We must make particular mention of the decarbonylation of furfural, and his process for the continuous hydrogenation of the resulting furan to tetrahydrofuran; under the conditions found the hydrogenation catalyst is active for a very long time. Exceptional interest is presented by his work on the preparation of butyl alcohol from synthetic rubber wastes and on the synthesis of excellent plasticizers or of starting materials for the preparation of plasticizers.

Special Subject "Chemistry of Macromolecular Compounds"

The new corresponding member Vasily Vladimirovich Korshak works on the chemistry of macromolecular compounds. V. V. Korshak combines in excellent fashion the solution of problems of great theoretical importance with the practical application of the results obtained. Most of his researches are concerned with macromolecular compounds, and are mainly devoted to the study of polycondensation processes leading to the formation of various polymers. Korshak and his coworkers have, for example, studied the polycondensation of dicarboxylic acids with diamines, glycols, and amino alcohols, and also of dichloroalkanes with aromatic hydrocarbons: he has found a new type of polycondensation reaction, namely, the transarylation of diarylalkanes in presence of catalysts. On the basis of the results of a large number of experimental investigations, Korshak has constructed a theory of linear polycondensation, which is in good agreement with the experimental results, explains the regularities observed in polycondensation processes, and enables the course of these processes to be controlled. As a result of his study of the polycondensation of dicarboxylic acids with diamines, polyamide resins were obtained, and these are soluble in organic solvents and are very promising for application as adhesives, lacquers, etc. Study of the polycondensation of dicarboxylic acids and their esters with glycols has led to the preparation of polyester resins having good mechanical and dielectric properties. Korshak has established the basic laws of the reactions leading to the formation of polyesters, and these laws are in close accord with the theory of linear polycondensation developed on the basis of his studies of the polycondensation of dicarboxylic acids with diamines. The results of some of Korshak's studies of polymerization have enabled certain generalizations to be made concerning the effect

of the sizes and number of substituents on the tendency of unsaturated compounds to polymerize.

Special Subject "Radiochemistry"

The new corresponding member Boris Petrovich Nikolsky has made original scientific investigations in a number of branches of physical chemistry. His main line of work has been associated with the experimental and theoretical study of ion exchange in heterogeneous systems. Nikolsky was the first to make extensive application of physicochemical methods of analysis in agricultural chemistry, and he initiated fundamental investigations, which are being successfully developed by the school of investigators that he has created. Of great importance is the development by Nikolsky of complex methods for the study of electrolytes in soil extracts: the extensive and accurate results obtained form the basis of his theory of ion exchange in soils. By a generalization from the results of studies on ion exchange a general classification of ion-exchange phenomena into three main types was evolved, and in these the cases of exchange by adsorptional and by chemical mechanisms appeared as limiting cases. For these types of exchange statistical and thermodynamical theories were evolved. Nikolsky gave a general equation covering all cases of ion exchange. These investigations are of importance also from the point of view of the double-layer concept, which was extended to nonmetallic systems (ion-exchange systems). Great scientific interest is presented by the theory that Nikolsky developed for the glass electrode, which is based on thorough experimental investigations and the theory of ion exchange advanced previously. In the majority of these investigations Nikolsky made extensive application of radiochemical methods, a field in which he is recognized specialist. Among other studies, his investigations on the physical chemistry of natural waters are of considerable importance: use of more accurate (in some cases, new) methods of investigation enabled a correlation to be established between the salt composition of natural waters and their physicochemical properties, particularly the pH.

Special Subject "Analytical Chemistry"

The investigational work of the new corresponding member Ivan Pavlovich Alimarin has taken three main directions: the development and improvement of methods for the analysis of minerals and ores; investigations on the analytical chemistry of widely diffused and rare elements; and the development and improvement of methods of micro and ultramicro analysis. His earliest work was related with the search for new methods, having greater speed and accuracy, for the analysis of mineral products; for example, the colorimetric determination of silicic acid in presence of iron, phosphorus, fluorine, etc. He carried out a number of investigations on the analytical chemistry of boron and the rapid and accurate determination of it in silicate minerals and other mineral products. A number of his investigations was devoted to the qualitative and quantitative determination of fluorine in minerals and fluxes. He perfected a method for the determination of constitutional water in micas and other minerals; it was based on the reaction between silicates and sodium tungstate at high temperature. Alimarin set up some mobile field laboratories enabling geologists to carry out qualitative and approximate quantitative analyses of useful minerals under field conditions. Alimarin has paid special attention to questions relating to the determination of elements present in trace amounts. In the solution of this important and difficult problem of analytical chemistry he has made extensive use of various physical and physicochemical methods of investigation, such as spectrum and X-ray-spectrum analysis, photocolorimetry, polarography, amperometry, electron microscopy, and labeled atoms. Alimarin has proposed a scheme for the analysis of micro quantities of minerals, slag occlusions, and the products of mineral synthesis in which a specially developed apparatus and analytical procedure is applied to samples of material weighing 1-20 mg. In recent years Alimarin has successfully developed methods of ultramicrochemistry.

At a session of the Division of Chemical Sciences held on October 19, 1953, papers were read by Academician I. L. Knunyants on "Investigations on Mercapto Amino Acids" and Corr. Memb. Acad. Sci. USSR A. P. Terent'yev on "Investigations on Functional Organic Analysis".

At a meeting of the Division held on October 24, 1953, in connection with the termination of his period of office, Academician Mikhail Mikhailovich Dubinin was again elected as Academician-Secretary of the Division.

At a general meeting of the Academy of Sciences of the USSR held on October 26, 1953, Academician M. M. Dubinin was elected as member of the Presidium of the Academy of Sciences of the USSR and his election as Academician-Secretary of the Division of Chemical Sciences of the Academy was confirmed.

A. E. CHICHIBABIN'S "FUNDAMENTAL PRINCIPLES OF ORGANIC CHEMISTRY", VOLUME I

I. L. Knunyants

Soviet chemical literature includes a number of textbooks on organic chemistry that have played important parts in the training of specialists in this branch of chemistry. Among such textbooks a leading place is occupied by A. E. Chichibabin's widely known "Fundamental Principles of Organic Chemistry", the last edition of which appeared in 1932 and was translated into foreign languages. In this book intelligent choice of factual material is combined with a deep and vigorous exposition.

Both from the methodological and scientific points of view, A. E. Chichibabin's book is generally acknowledged to be one of the best in world chemical literature. It gives an exceptionally competent exposition of the mutual relationships between the various classes of organic compounds. It teaches dialectics in action and develops the chemist's mode of thought in the student. All this helps in the rapid acquiring of the colossal factual material of organic chemistry and builds it up into a systematic, easily remembered system.

In the twenty years that have passed, however, Chichibabin's book has in many respects become out of date. In recent years organic chemistry has made considerable progress, and many of the concepts developed earlier have been changed. These are concerned mainly with new reactions and transformations of hydrocarbons and aliphatic derivatives, on the basis of which new branches of chemical industry have arisen. It is natural that the exceptional qualities of this textbook should make it necessary to bring out a new edition, in which it would be necessary to revise and supplement it, mainly with respect to factual material and its theoretical treatment. This work has now been done by the State Chemical Literature Press, with the participation of a large group of Soviet scientists, and Volume I of the book (Acyclic Compounds) has now appeared under the editorship of Prof. P. G. Sergeev.

In the new edition the order of exposition and a great part of the factual material are retained. The principal sections are supplemented by new material that reflects the attainments of organic chemistry in the last two decades. There is, for example, a treatment of recent developments in the chemistry of paraffin hydrocarbons, of new methods of using acetylenic hydrocarbons, and of progress in the chemistry of macromolecular compounds, including natural polymers. Modern views on the mechanisms of the more important reactions are given, and an adequate account is given of the possibilities of physicochemical methods and other modern methods of organic chemistry, and of results of their application. Some important sections have been practically rewritten, for example, the chemistry of carbohydrates. Many sections have been radically revised, e. g., the chemistry of amino acids and proteins, the polymerization of unsaturated compounds, X-ray analysis, and the Walden inversion.

In connection with the development and successful application of electronic concepts in organic chemistry, a new theoretical introduction is given containing an objective historical review of the origins and development of theoretical concepts in organic chemistry. A particularly detailed exposition is given of the origin and development of A. M. Butlerov's theory of chemical structure. Much attention is devoted to modern views on chemical structure and the mutual effects of atoms in molecules. The scientific invalidity of the concepts of resonance and mesomerism are demonstrated. The additional matter in the theoretical introduction is written in full accord with the decisions of the conference on questions of the theory of chemical structure in organic chemistry held by the Division of Chemical Sciences in 1951 and with the decisions of the conference of organic chemists held by the Division of Chemical Sciences in 1953. In general, with the exception of some minor errors, this section is written well and carries the reader up to the present level of theory. Apart from the material expounded in the theoretical introduction, there are theoretical treatments in the main text relating to the subjects treated there.

Organic chemistry is a science on which many branches of industry are based, and the introduction into the textbook of information concerning the technological significance of particular reactions and the main methods of processing and utilizing organic substances must be regarded as correct. The book, of course, does not give an exposition of the technology of any particular manufacturing process, but the possibility in principle of technical syntheses is given adequate treatment (the chemical treatment of petroleum hydrocarbons, the preparation of synthetic rubber and other high polymers from unsaturated compounds, the manufacture of polyamide resins and of artificial and synthetic fibers, etc).

The book is not free from defects and omissions. Among the main defects of the book as a textbook is its considerable size. The increase in size results mainly from the added material in the introduction, the inclusion of tables of the properties of the homologs in individual classes and of short biographies of chemists, and the extension of chapters on carbohydrates and proteins. These increases in size are partially compensated for by the considerable shortening of the sections on the qualitative and quantitative analysis of organic compounds; also, the section on complex compounds has been removed. It must be pointed out also that individual reactions have not generally been given detailed interpretation in terms of electronic concepts, although this should have been done in many cases. The weakest section is that on proteins; here not only is the student presented with some doubtful facts, but there are a few errors in nomenclature (haloalkyl, instead of alkyl halide, etc.). A particularly unsatisfactory feature for a textbook is formed by a number of misstatements and factual errors, which, unfortunately, are rather numerous.

For example, on p. 422, it is stated that in the hydration of ethylene oxide polyethyleneglycols are formed as intermediate products. This misstatement – "intermediate product" instead of "by-product" – can lead to an incorrect understanding of the process. On the previous page the same question is treated incorrectly. On p. 76, an unsatisfactory example is given in illustration of pure geometric isomerism in absence of an asymmetric carbon atom. On pp. 188 and 414, contradictory information is given concerning the application of tetrachloroethane. On. p. 335 an unsatisfactory treatment is given of the use of olefins. On p. 337, haloalkyl is written instead of alkyl halide. In the supplementary notes on p. 424, reference is made to rubberized fabrics impregnated in drying oils, which are not manufactured. On p. 241, an incorrect formula is given for Rongalite, the sulfur being united to the hydroxymethyl group through an oxygen atom. On p. 337, "correctnesses" is written instead of "laws". On p. 300, NN-dichloroamines are referred to as derivatives of nitrogen trichloride. On p. 301, the bonds are incorrectly represented in alkylarsonic, alkylphosphonic etc. acids. Some of the concepts introduced into the textbook, e. g., the coordinate link, are not provided with a satisfactory theoretical basis. In general, however, the work of the team of chemists on the revision and extension of Chichibabin's book is very praiseworthy. It is to be regretted that in the course of the last twenty years, not a single textbook has been issued that corresponds, in its methodological significance and theoretical level, with the contemporary state of organic chemistry. The present edition of Chichibabin in the main fills this gap. The appearance of Volume I of the revised "Fundamental Principles of Organic Chemistry" is an important event for specialists in organic chemistry, and also for chemistry students, who have at last been provided with a good modern textbook.

LOW-TEMPERATURE MODIFICATIONS OF AMMONIUM NITRATE, AND ITS COOLING AND QUENCHING

S. I. Volfkovich, S. M. Rubinchik, and V. M. Kozhin

In addition to the four crystalline modifications of ammonium nitrate that exist at normal pressure and at temperatures above 0° (I, cubic, 169-125°; II, tetragonal, 125-84.5°; III, β-rhombic, 84.5-32.4°; IV, α-rhombic, 32.4° to − 16°), there are known also one modification that exists below 0° (V, tetragonal, stable below − 16°) and one modification that exists at pressures higher than 9000 kg/sq. cm and temperatures above 169.2°.

There are indications in the literature that a transformation of ammonium nitrate occurs also in the region − 50° to − 65°. Hendricks and coworkers [1], who detected a small anomalous change in the specific volume at − 50°, point out that the X-ray diagrams for ammonium nitrate powder at − 33° and − 78° are very similar. Crenshaw and Ritter [2], who studied the variation of the specific heat of NH_4NO_3 with temperature, obtained a maximum on the specific heat − temperature curve at − 60.4°. In an analysis of these results, Meerman [3] pointed out quite rightly that the curve should have had a maximum at − 16°, since there can be no doubt in the existence of a transition at − 16° (IV ⇌ V); but the authors concerned detected no maximum at − 16°. Meerman considers that there is no transition at − 60.4°, but only retardation of the establishment of equilibrium, which is observed for a number of ammonium salts at low temperatures. Jaffray [4], using the differential-thermal method, found the transition temperature of NH_4NO_3 to be − 57° to − 60°. He noted also a transition in the region − 150° to − 160°, but mentioned this only in passing. Volkringer and coworkers [5] have noted an anomaly in the Raman spectra of ammonium nitrate between − 75° and − 192°.

In view of the meager study that has been devoted to the behavior of ammonium nitrate at low temperatures, we have investigated the transformations of this salt with the aid of differential thermal analysis, microcinematography, and X-ray analysis. Microcinematography of the polymorphic changes of ammonium nitrate was first carried out in the range 170-20° in 1940 by one of the authors of the present paper, working with Glazova [6] in the Laboratory of Scientific and Applied Photography and Cinematography of the Academy of Sciences of the USSR.

EXPERIMENTAL

In the present investigation we have studied the behavior of the salt when cooled to − 196°. We have made use of Tsurinov and Volnova's universal cooling and heating stage in this work, the cooling agent employed being liquid nitrogen. The temperature was determined by means of a fine thermocouple (platinum and platinum-rhodium; d = 0.1 mm).

A 0.001-0.002 g sample of dry ammonium nitrate was placed on a slide, covered with a cover glass, and carefully heated to melting. The fused ammonium nitrate was slowly cooled (1-1.5° per minute) under the microscope in polarized light (magnification 8 x 10), and the four transitions to crystalline modifications were clearly perceived (Figures 1-4).

$$\text{Melt} \xrightarrow[169°]{} \text{I} \xrightarrow[125°]{} \text{II} \xrightarrow[84.5°]{} \text{III} \xrightarrow[32°]{} \text{IV}$$

When the rate of cooling exceeded 2° per minute, only three transitions were observed:

$$\text{Melt} \xrightarrow[169°]{} \text{I} \xrightarrow[125°]{} \text{II} \xrightarrow[50°]{} \text{IV}$$

i.e., when cooling is at more than 2° per minute the modification III is not detected, and instead of the points

84.5° and 32°, the point 50° is found. This transition was recorded on cinecolor film, a very clear picture being obtained.

The large polyhedra of II were converted into a needlelike polycrystal (Fig. 5). No visible changes occurred in the polycrystal when it was preserved in a desiccator for 14 days.

In order to clarify the meaning of the pictures obtained by microcinematography, we took cooling curves. On these curves (Figures 6-9), which were plotted for various cooling rates (1.5-30° per minute) and for samples of 0.02-0.15 g, the same breaks were always obtained; they corresponded to the transitions:

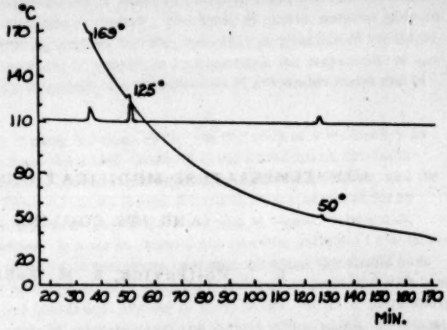

Fig. 6. Cooling curve for NH_4NO_3: R_D* 900 ohms; R_d 740 ohms; cooling rate 1.5°/min; wt. 0.02 g.

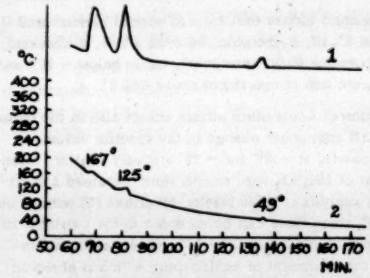

Fig. 7. Cooling curve for NH_4NO_3: R_D* 2000 ohms; R_d 150 ohms; cooling rate 1.9°/min; wt. 0.15 g. 1) Differential plot; 2) direct plot.

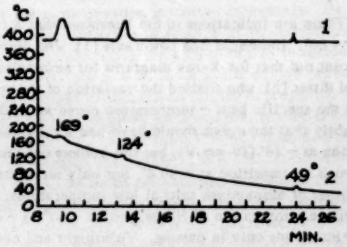

Fig. 8. Cooling curve for NH_4NO_3: R_D* 2000 ohms; R_d 150 ohms; cooling rate 8.3°/min; wt. 0.03 g. 1) Differential plot; 2) direct plot.

$$\text{Melt} \xrightarrow[169^\circ]{} \text{I} \xrightarrow[125^\circ]{} \text{II} \xrightarrow[50^\circ]{} \text{IV}$$

We were unable to plot the cooling curve for a very small sample of fused ammonium nitrate (0.001-0.002 g, as we took for the microscopic investigation), in which all four transitions should have been found. We carried out trials in which the sample was heated at above 125°, but below the melting point, and was then cooled; the transition $\text{II} \xrightarrow[50^\circ]{} \text{IV}$ was again found (Figures 10 and 11). But we obtained a quite clear indication of the transition $\text{III} \xrightarrow[84.5^\circ]{} \text{IV}$ on the cooling curves of ammonium nitrate preheated at below 125° with samples of the order of 0.02-0.15 g (Figures 12 and 13).

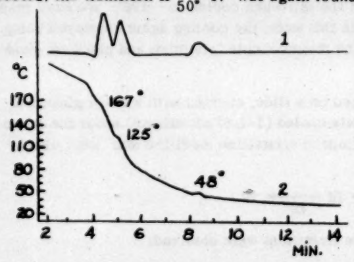

Fig. 9. Cooling curve for NH_4NO_3: R_D 1000 ohms; R_d 100 ohms; cooling rate 30°/min; wt. 0.05 g. 1) differential plot; 2) direct plot.

The transition at 50° was studied microscopically by Bowen [7], who stated that the transition occurs very readily, both when cooling, and also when heating. According to Hendricks and coworkers [1], the transformation can be repeated many times by heating and cooling, so long as the sample is dry and in the form of a thin film. In a thick layer Modification III is formed after 3-4 transitions. Tiemeyer [8] confirmed this transition by X-ray analysis. He pointed out that it is impossible to repeat the transition $\text{II} \rightleftharpoons \text{IV}$ a large number of times by repeated alteration of the temperature, since

* R_D = Resistance direct; R_d = Resistance differential.

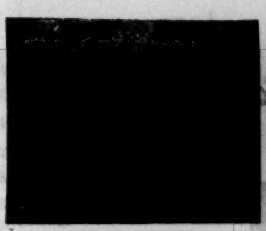

Fig. 1. Modification I, cubic. The darkening on the right is incipient I ⟶ II transition.

Fig. 2. Modification II.

Fig. 3. Modification III.

Fig. 4. Modification IV.

Fig. 5. Polycrystal of NH_4NO_3 after II ⟶ IV transition.

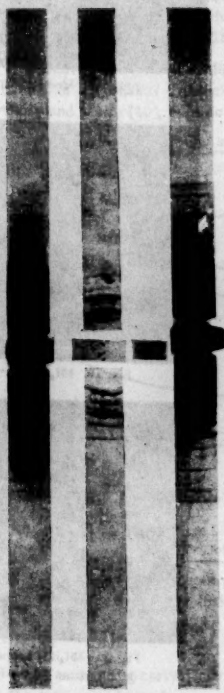

Fig. 22. X-Ray diagrams of NH_4NO_3: a) Modification IV; b) Modification V; c) Modification VII.

Fig. 23. X-Ray diagram of NH_4NO_3 quenched at −196°.

Fig. 24. X-Ray diagram of NH_4NO_3 quenched at − 20°.

Note: Figs. 18, 19, and 20 in the original are color photographs, which can not be reproduced in color by the process used for publication of this translation. The predominant colors in each photograph are therefore indicated on the black-and-white reproductions below. Publisher.

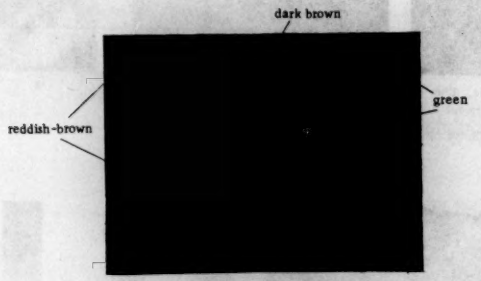

Fig. 18. Modification V.

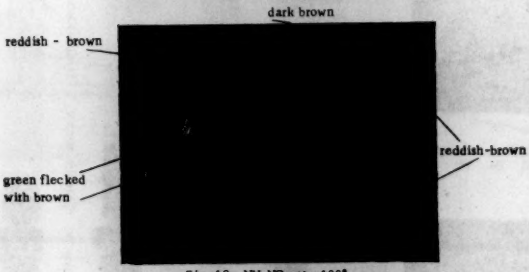

Fig. 19. NH_4NO_3 at −100°.

Fig. 20. NH_4NO_3 below −170°
(Modification VII has formed).

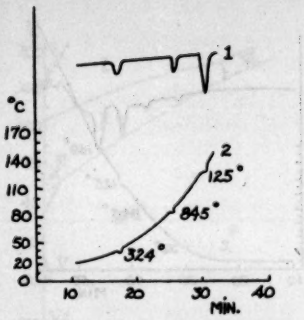

Fig. 10. Heating curve for NH_4NO_3; R_D 1000 ohms; R_d 100 ohms; heating rate 7°/min; wt. 0.03 g. 1) Differential plot; 2) direct plot.

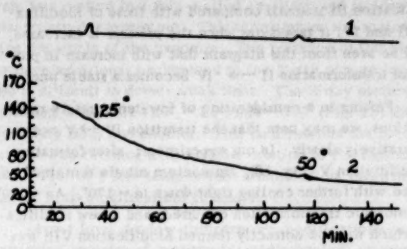

Fig. 11. Cooling curve for NH_4NO_3: R_D 1000 ohms; R_d 100 ohms; cooling rate 1°/min; wt. 0.03 g. 1) Differential plot; 2) direct plot.

polycrystalline transformation occurs with formation of Modification III. One of us, working with Glazova [6] has observed a transition of NH_4NO_3, both during cooling and during heating, in the region 47-55° (in addition to the transitions at 125°, 84.5°, 32.4°, and − 16°).

Nikonova [9] determined the II ⟶ IV transition point thermographically, the cooling curves being plotted by the aid of a Kurnakov pyrometer. On heating curves, she did not observe this transition. Some investigators, e.g. Early and Lowry [10], consider that we are concerned here not with a transition, but with supercooling of Modification III.

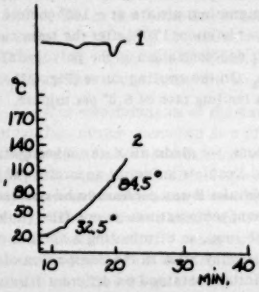

Fig. 12. Heating curve for NH_4NO_3: R_D 1000 ohms; R_d 100 ohms; heating rate 8.8°/min; wt. 0.02 g. 1) Differential plot; 2) direct plot.

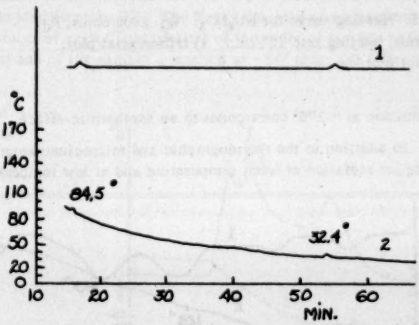

Fig. 13. Cooling curve for NH_4NO_3: R_D 1000 ohms; R_d 100 ohms; cooling rate 1.4°/min; wt. 0.02 g. 1) Differential plot; 2) direct plot.

We must point out that on our heating curves (Figures 14-16), which were plotted for various rates of heating (7.3-60°/min.), four distinct breaks are always found, corresponding to the following four transformations:

$$IV \xrightarrow[32.4°]{} III \xrightarrow[84.5°]{} II \xrightarrow[125°]{} I \xrightarrow[169°]{} \text{melt}$$

We, like Nikonova, never observed the transition IV ⟶ II on heating curves, even when samples that had just (10-20 minutes before) undergone the transformation $II \xrightarrow[50°]{} IV$ were heated.

It will be seen from the pressure-temperature diagram of the fields of existence of modifications of ammonium nitrate constructed by Bridgman [11] (Fig. 17) from his own results and those of other investigators

(Modification VII has been inserted by us) that the field of Modification III is small compared with those of Modifications II and IV; it tapers out when the pressure is increased. It will be seen from this diagram that with increase in pressure the transformation II ⟶ IV becomes a stable one.

Passing to a consideration of low-temperature transformations, we may note that the transition IV ⟶ V occurs comparatively slowly. In our experiments, after formation of Modification V (Fig. 18), ammonium nitrate remained unchanged with further cooling right down to − 170°. At − 170° a polymorphic transformation occurred, and a new modification, which may be correctly termed Modification VII, was formed.

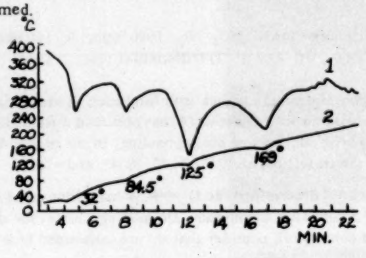

Fig. 15. Heating curve for NH_4NO_3: R_p 2000 ohms; R_d 150 ohms; heating rate 12°/min. 1) Differential plot; 2) direct plot.

the transition at − 170° corresponds to an exothermic effect.

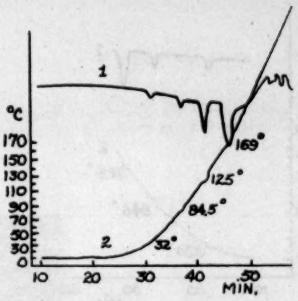

Fig. 14. Heating curve for NH_4NO_3: R_p 1000 ohms; R_d 100 ohms; heating rate 7.3° per minute; wt. 0.03 g. 1) Differential plot; 2) direct plot.

At the polymorphic transition point the optical properties of the polycrystal were altered, and the interference colors observed by transmitted polarized light were changed. In Figures 19 and 20 we give color photomicrographs of the polycrystal of ammonium nitrate at − 100° (before the transition) and below − 170° (after the transition).* The peculiar decolorization of the polycrystal will be seen. On the cooling curve (Fig. 21), plotted for a cooling rate of 6.3° per minute,

In addition to the thermographic and microcinematographic investigations, we made an X-ray investigation with copper radiation at room temperature and at low temperatures.** We used Kozhin's universal apparatus [12], which permits X-ray pictures to be obtained at different temperatures on one film (holder R = 28.65 mm), so eliminating a number of errors that may arise in the comparison of X-ray pictures obtained on different films.

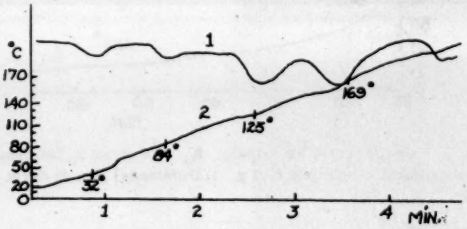

Fig. 16. Heating curve for NH_4NO_3: R_p 1000 ohms; R_d 100 ohms; heating rate 60°/min; wt. 0.03 g. 1) Differential plot; 2) direct plot.

The sample of ammonium nitrate, diameter 1 mm and height 5 mm, was set up on a goniometric head and covered with a cellophane thimble, diameter 8 mm and height 10 mm, which is necessary for the mechanical protection of the sample from the fine stream of cooling agent (liquid nitrogen or a mixture of alcohol and solid carbon dioxide). The sample attained the temperature of the coolant (− 196° for liquid nitrogen, − 20° for a mixture of alcohol and solid carbon dioxide) after five minutes' treatment (the temperature of the sample was measured with a copper-constantan thermocouple).

* The color photomicrographs are reproduced in black and white (see plate, page 170).

** The investigation was carried out in the X-ray Structure Laboratory of the Institute of Organic Chemistry of the Academy of Sciences of the USSR.

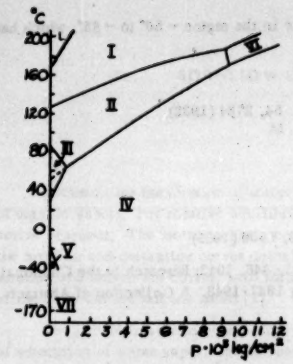

Fig. 17. Fields of existence of NH_4NO_3 modifications.

In the X-ray study of quenched samples, the ammonium nitrate was melted in a thin-walled capillary and rapidly cooled to the required temperature. This temperature was maintained during the whole of the exposure. The presence of the glass capillary gave additional background to the X-ray picture, and this made it difficult to detect weak lines. The X-ray pictures for ammonium nitrate at +20°, − 20°, and − 196° (Fig. 22) differ appreciably from one another. This confirms the microcinematographic and thermographic results relating to the existence at below − 170° of a low-temperature modification, differing in its structure from Modifications IV and V.

Apart from the low-temperature modifications, we have investigated samples of quenched (rapidly cooled) ammonium nitrate by means of microcinematography; such work is of interest in connection with the better physico-mechanical properties of a salt obtained in this way. Volfkovich and Glazova [6] have shown that the quenched product is of lower hygroscopicity and has less tendency to cake. Their results indicating that more than one phase is formed are not contradicted by the present investigation. The X-ray pictures of ammonium nitrate quenched at − 196° (Fig. 23), and not quenched, but photographed at − 196° (Fig. 22c) are somewhat similar with respect to the distribution of the lines.

The X-ray diagrams of samples quenched at − 196° (Fig. 23) and not quenched but photographed at + 20° (Fig. 22a) are also similar with respect to the distribution of interference lines. It is probable that quenching to − 196° results in the formation of Modification IV and Modification VII. The X-ray diagram of ammonium nitrate quenched at − 20° (Fig. 24) shows that the sample consists of crystallites (grains) of the order of not less than 10^{-2}-10^{-3} cm. The structures of Modification V (Fig. 22b) and of the sample quenched at − 20° (Fig. 24) differ in that the crystallites of the latter are larger.

Our measurements of the extrusion pressure of ammonium nitrate quenched at − 20° showed that this is lower than that of Modification V by a factor of about 3.5. Ammonium nitrate quenched at − 20° probably contains Modification V and possibly also IV, but not III, since we have already shown that at cooling rates of greater than 1.5° per minute Modification III cannot be detected on the cooling curves even for samples of 0.02-0.03 g.

SUMMARY

1. The existence of a low-temperature modification of ammonium nitrate at below − 170° has been confirmed by microcinematographic, X-ray structure, and thermographic analysis; it may be suitably named Crystalline Modification VII.

2. When fused ammonium nitrate is cooled at a rate of more than 2° per minute, metastable transformation of Modification II to Modification IV occurs, but the reverse change is not observed when the temperature is raised.

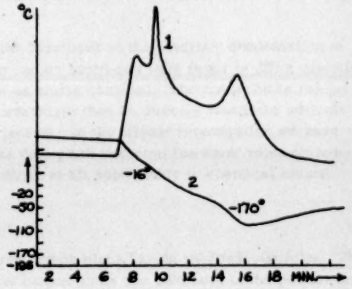

Fig. 21. Cooling curve for NH_4NO_3: R_D 2300 ohms; R_d 1200 ohms; cooling rate 6.3°/min. 1) Differential plot; 2) direct plot.

3. Ammonium nitrate quenched at − 20° consists mainly of Modifications V and IV. As can be seen from cooling curves plotted for different cooling rates, Modification III will be absent. Ammonium nitrate quenched at

– 196° consists of Modifications IV and VII.

4. We have not detected the transformation of ammonium nitrate in the region – 50° to – 65°, which has been found by some workers.

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Received September 17, 1953.

SORPTION OF WATER VAPOR BY ACTIVE CHARCOALS

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Isotherms for the sorption of water vapor by active charcoals differ greatly in form from those for the sorption of organic vapors. For relative equilibrium pressures in the region of 0.4, water vapor is not adsorbed strongly by active charcoal. The isotherm has a concave form, and for ashless charcoals, e.g., that prepared from sucrose, the sorption and desorption curves coincide in this region. At higher relative pressures, there are sharp rises in the sorption and desorption curves, with formation of the hysteresis loop characteristic of water vapor when the pores of the charcoal are not too small [1].

The initial, reversible part of the isotherm, up to the point where hysteresis begins, represents the process of adsorption of water vapor; the irreversible, steeply rising part of the curve is generally associated with capillary condensation of vapor. Our previous detailed investigation of the isotherms for the sorption and desorption of water vapor at the surface of ashless sucrose charcoals activated in varying degree led to the formulation of a working hypothesis, according to which the sorption of water vapor by active charcoals is the sum of two processes: adsorption and capillary condensation [1]. It was supposed that the main condition for the occurrence of capillary condensation in the pores of the charcoal was the formation of a condensed monomolecular adsorbed layer as a result of a phase transition of the two-dimensional vapor at a definite equilibrium pressure for surface sites of constant heat of adsorption. This condition may be observed at relative vapor pressures higher than those calculated from the pore dimensions by Thomson's equation. The process of capillary condensation then takes on a forced character.

Juhola and Wiig conclude from the results of their experiments that in the hysteresis region the sorption and desorption curves of the isotherm correspond to capillary condensation and evaporation of water for different wetting angles, namely, $\cos\theta = 0.49$ for desorption and $\cos\theta = 0.28$ for sorption [2,3]. With such an assumption it becomes possible, from the theory of capillary condensation and the sorption and desorption isotherms for water vapor, to calculate structure curves for active charcoals and differential curves for the distribution of pore volume according to pore radius.

We should, of course, be provided with a sounder basis for the hypothesis of the capillary condensation of water vapor if the sorption isotherms for water vapor on nonporous carbon adsorbents were found to differ essentially in their character in their central parts from those for water vapor on active charcoal. The sharp rise in the isotherms for active charcoals in the 0.4-0.6 range of relative pressures might then be directly associated with the presence of a porous structure and with a capillary-condensation process. In the present investigation we have undertaken the task of making a comparative study of sorption and desorption isotherms for water vapor on nonporous and porous carbon adsorbents having surfaces that cannot differ at all appreciably in chemical nature.

EXPERIMENTAL

As our nonporous carbon adsorbent, we took thermally treated carbon black having spherical particles. The carbon black was heated in a vacuum at 950°. In the experiments the carbon black was used both in the powder form and as briquets prepared without the aid of binding materials.

The sorption and desorption isotherms for benzene and water vapors were determined by the sorption-balance vacuum method [4]. The preliminary evacuation of the adsorbents was effected by means of a three-stage mercury vapor pump; it was continued for six hours at 450°. In the sorption and desorption experiments, particular attention was paid to the attainment of an equilibrium state.

Sorption and desorption isotherms for benzene vapor on thermally treated carbon black powder at 20° are shown in Fig. 1. For relative pressures of up to 0.78, the adsorption and desorption points are closely represented by a single curve. At higher relative pressures, there is a sharp rise in the sorption curve, mainly due to capillary condensation of benzene vapor in the spaces formed between the carbon black particles. The desorption isotherm is now not coincident with the sorption isotherm, and the two curves form the hysteresis loop that is characteristic of capillary condensation. The limit of sorption is at 11.6 mmole/g.

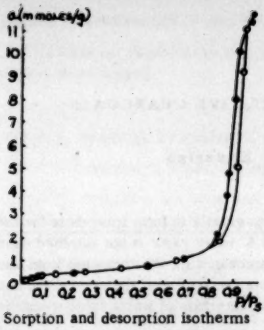

Fig. 1. Sorption and desorption isotherms for benzene vapor on carbon black at 20°.

For briquet and powder-form carbon blacks the adsorption isotherms coincide up to a relative pressure of 0.95, when the adsorption is 7 mmole/g. Over the pressure range 0.95-1.00 the sorption isotherm for the briquet moves over to the right, and the limit of sorption is only 8.95 mmole/g. In its steep region, the desorption isotherm for the same carbon black is parallel to the desorption isotherm for carbon black powder, but is displaced by 0.25 relative pressure units in the direction of lower pressures. Compression of carbon black therefore results in a reduction of the volume of free spaces between the particles, increase in the number of contacts, and to some reduction in the dimensions of the spaces formed at the points of contact. In the adsorption region the equilibrium is reversible, and the adsorption and desorption points for both samples of carbon black are closely represented by a single curve Hence, the powder and briquet forms of carbon black do not differ in their adsorption properties, and therefore not in their specific surfaces.

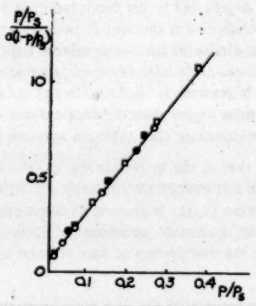

Fig. 2. Adsorption and desorption isotherms for benzene vapor at 20° in linear form. Adsorption: ○ – carbon black powder; □ – carbon black briquet. Desorption: ● – carbon black powder; ■ – carbon black briquet.

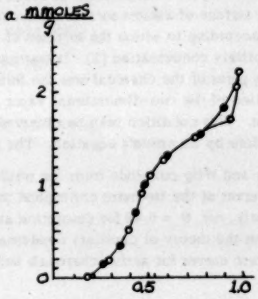

Fig. 3. Sorption and desorption isotherms for water vapor on carbon black at 20°: ○ – adsorption; ● – desorption.

In Fig. 2, the experimental results for the adsorption of benzene vapor at 20° for powder-form and briquet carbon blacks are represented in linear form in accordance with the adsorption-isotherm equation of Brunauer, Emmett, and Teller [5]. The value of the adsorption of benzene vapor calculated for a compact monolayer on carbon black from the constants of the equation is a_m = 0.365 mmole/g. If we assume, in accord with the results of Kiselev, Karnaukhov, and Khrapova [6], that the most probable value of the molecular area of benzene in a monolayer for a similar sample of carbon black is 46.5 A^2 (not differing greatly from the value of 41 A^2, found by Smith and Pearce [7]), then the specific surface of the investigated sample of carbon black will be 103 sq.m/g. A statistical treatment of numerous electron-microscope photographs, which was carried out in our laboratory by Radushkevich and Lukyanovich, has led to a value of 98 sq.m/g for the specific surface of the carbon black. The close agreement of the results of adsorption and electron-microscope measurements shows that the sample of carbon black was indeed a nonporous carbon adsorbent.

Fig. 3 represents sorption and desorption isotherms for water vapor on carbon black at 20°, as determined by the vacuum sorption-balance method. In the range of low relative pressures, the adsorption of water vapor is immeasurably small. In the middle range of relative pressures adsorption is reversible, and there is a steep rise in the isotherm. The inflexion point on the curve at a relative pressure of 0.55 corresponds to an adsorption of a = 1.20 mmole/g. As limiting sorption is approached, there is again a sharp rise in the isotherm, and in this range of relative pressures the sorption and desorption isotherms do not coincide, a characteristic hysteresis loop being formed.

According to Harkins and Jura the molecular area in a compact water monolayer is 14.8 A^2 [8]. For a specific surface in the carbon black of 103 sq.m/g, completion of a monolayer corresponds to an adsorption of $a_m = 1.35$ mmole/g. This value corresponds almost exactly to the completion of the main rise of the isotherm and its point of inflection at a = 1.20 mmole/g. Hence, for carbon black, and for relative pressure of up to 0.55, adsorption is on the average monomolecular. Polymolecular adsorption at higher pressures is complicated by the closeness to saturation for capillary condensation of water vapor in the spaces formed by spherical carbon black particles arrayed in contact with one another.

As our porous carbon adsorbents, we took four samples of active wood charcoal, prepared with the assistance of Chepurnoi [9]. The conditions of its thermal treatment at 950° were exactly the same as those used for carbon black. In general character, the sorption isotherms for water vapor did not differ from those obtained on carbon black. The main rise of the isotherm was in the 0.4-0.6 range of relative pressures, both for active charcoals and for carbon black.

By way of example, sorption isotherms for water vapor on carbon black and on charcoal No. 1 are shown, with different scales along the ordinate axis, in Fig. 4. The regions of sharp rise are somewhat displaced from one another, which is to be explained by a small difference in the properties of the surfaces of active charcoal and carbon black. The points of inflexion on both isotherms at a relative pressure of about 0.55 evidently correspond to completion of the formation of a compact monomolecular adsorbed layer. After this, the surface properties of the carbon black and active charcoal become almost identical, and the adsorption isotherms coincide over the 0.55-0.95 range of relative pressures, in which polymolecular adsorption occurs.

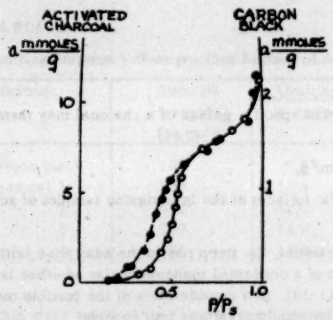

Fig. 4. Sorption isotherms for water at 20° on carbon black (●) and activated charcoal (○).

The coincidence of these adjusted isotherms in the range of relative pressures indicated is evidence of the mathematical affinity of the curves.

The mathematical condition for the affinity of the isotherms may be written:

$$a_1 = \underline{f}(p/p_s); \quad (1)$$

$$a_2 = k\underline{f}(p/p_s), \quad (2)$$

where a_1 is the adsorption on carbon black; a_2 is the adsorption on active charcoal; $\underline{k}$ is the affinity coefficient. Expressing the isotherm equations in the form of inverse functions, we have:

$$p/p_s = \varphi(a_1) \quad (3)$$

$$p/p_s = \varphi(a_2/k) \quad (4)$$

and for the adsorption values a_1 and a_2 corresponding to identical relative pressures in the range under consideration, taking into account that the function φ is not periodic, we obtain:

$$a_2 = ka_1, \quad (5)$$

i.e., a linear relation between a_2 and a_1.

The graphs in Fig. 5 will serve as proof of the affinity of the adsorption isotherms for water vapor on carbon black and on the studied samples of active charcoal in the 0.55-0.95 range of relative pressures; the points correspond to the adsorption values for each of the active charcoals and the carbon black at identical relative pressures. These points, obtained by interpolation on the water vapor sorption isotherms for each sample of charcoal, fit closely to straight lines passing through the origin. With the chosen disposition of the axes of coordinates, the reciprocals of the slopes of the lines are affinity coefficients for the isotherms.

In Table 1 we give the affinity coefficients of the isotherms for the region of polymolecular adsorption, as determined from the graphs in Fig. 5. Since dispersion forces do not play a determining part in this region of water vapor sorption, the porous structure of the adsorbent cannot have a significant effect on the adsorption [10]. Hence, the affinity of the isotherms in the 0.55-0.95 range of relative pressures is evidence for the coincidence of the absolute adsorption isotherms, in the construction of which adsorption values are expressed in terms of unit area of adsorbent. Thus, in the case under consideration, the affinity coefficient is equal to the ratio of the

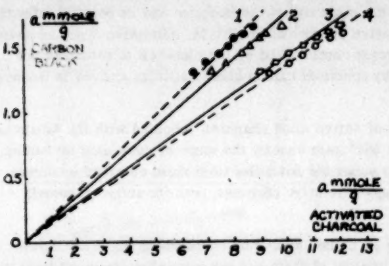

Fig. 5. Relation between values of the sorption of water vapor at 20° on carbon black and on active charcoals (nos. 1-4) for identical equilibrium pressures.

TABLE 1

Affinity Coefficients of Isotherms and Specific Surfaces of Active Charcoals

Adsorbent	Affinity coefficient of isotherm, $\underline{k}$	Specific surface, $\underline{s}$ (sq.m/g)
Carbon black	1.00	103
Charcoal 1	5.15	530
" 2	5.75	590
" 3	7.08	730
" 4	7.42	765

specific surface of the active charcoal to that of the carbon black. The specific surface of a charcoal may therefore be expressed by the formula:

$$s = 103 \cdot k \text{ sq.m/g},$$

(103 sq.m/g is the specific surface of the carbon black). The specific surfaces of the investigated samples of active charcoal, calculated in this way, are given in Table 1.

According to the concepts that we have developed in our laboratories, the steep rise in the adsorption isotherm for water vapor on carbon adsorbents is associated with the formation of a condensed monomolecular adsorbed layer, a major role in this process being the formation of hydrogen bonds [11-13]. In a consideration of the possible mechanism for the sorption of water vapor, it is necessary to take the nature of the adsorbent surface into account.

In our experiments, after thermal treatment at 950° the active charcoals and carbon black were brought into contact with air. Hence, as a result of activated adsorption (chemisorption), surface oxides were formed, and these could not be destroyed in the preliminary evacuation of the carbons at 450°. It may be supposed that, in the region of low equilibrium pressures, adsorption of water vapor is associated mainly with the formation of hydrogen bonds between adsorbed water molecules and surface oxides on the carbon adsorbents [13]. As a result of the relatively low energy of the hydrogen bond, adsorption is low.

Adsorbed water molecules form a special type of secondary adsorption centers, which may hold other molecules by hydrogen bonds. As a result of this, patches of a two-dimensional condensed phase appear as the pressure rises, these being formed of water molecules held by hydrogen bonds. The probability of the occurrence of this process will rise as the pressure increases up to a certain point, owing to increase in the number of adsorption centers. At a sufficiently high pressure the patches will merge, and a continuous condensed monomolecular layer will be formed. The steep rise in the isotherm in the middle range of relative pressures is probably to be associated with this peculiar process of the formation of two-dimensional patches of liquid, which proceeds until they merge together.

In considering the question of the stability of the associated complexes of water molecules in the form of patches of a condensed two-dimensional phase, which are formed on the surface of carbon adsorbents, two factors must be taken into account: the first is concerned with the surface oxides, which act as primary adsorption centers, and the second is concerned with the adsorption field, which is relatively weak in our case, and is due mainly to dispersion forces. Although water molecules are not associated in the gas phase since the thermal energy of movement is sufficient to break down complexes that form, the complexes are stabilized in the surface field of the adsorbent, and they become stable [12].

The increased adsorption potentials of dispersion forces in the fine pores of active charcoal increase still more the stability of these complexes of associated water molecules and make their formation possible at somewhat lower relative pressures in the gas phase. It is possible that it is this effect that causes the shift of the steep part of the sorption isotherm for water vapor toward lower pressures in a series of charcoals of various degrees of activation when we pass from relatively coarsely porous to more finely porous charcoals [1].

The nature of this shift requires more detailed study. In particular, it is important to evaluate the possible differences in the surface chemical properties of charcoals of various degrees of activation, i.e., having widely different carbonization treatments.

When the condensed monomolecular adsorbed layer has been formed, further rise in relative pressure results in the polymolecular adsorption of water vapor, which is complicated by capillary condensation when the porous structure of the active charcoal favors this process. In the case of the active charcoals that we have studied, capillary condensation comes into consideration when the main rise of the sorption isotherm, corresponding to the formation of a condensed monolayer, is complete. We may judge whether polymolecular adsorption or capillary condensation plays the determining role in the sorption of water vapor at relative pressures of greater than 0.55 by a consideration of the limiting sorption values expressed in relation to 1 sq.m of the charcoal surface. In the case of capillary condensation, the main factor determining the limiting sorption at a relative pressure of unity, will be the volume of fillable pores. It is difficult to imagine that this quantity will be directly proportional to the adsorbent surface. On the other hand, if polymolecular adsorption is of determining significance, the absolute values of the limiting sorption will lie close together for different charcoals. The results of the relevant calculations from the experimental data are given in Table 2.

TABLE 2

Limiting Sorption Values per Unit Surface of Active Charcoals

Adsorbent	Specific surface, s (sq.m/g)	Limiting sorption a_∞ (mmole/g)	$\alpha_\infty = a_\infty / s$ (mmole/sq.m)
Carbon black	103	2.21	0.021
Charcoal 1	530	11.3	0.021
" 2	590	12.6	0.021
" 3	730	14.9	0.020
" 4	765	15.8	0.021

The almost identical limiting values for the sorption of water vapor (α_∞) for nonporous carbon black and the samples of active charcoal examined indicate that, in the direct sorption process, the region of polymolecular adsorption extends right up to high relative pressures, approaching unity in value. In our cases of sorption, capillary condensation may play only a very small part. However, if as a result of polymolecular adsorption and, to some extent, capillary condensation with attainment of the sorption limit, even a part of the finer pores of the active charcoal is filled, then the possibility cannot be excluded that in the desorption process the emptying of the pores will occur over a certain range of relative pressures, in accord with the theory of capillary condensation. A more detailed study of this aspect of the sorption process will be made in our further investigations.

The basic idea, therefore, of our previously developed concepts concerning the sorption of water vapor; namely, the formation of a condensed adsorbed film as a necessary condition for the occurrence of the process of capillary condensation, remains unchanged [1]. The described process, in which two-dimensional patches of water molecules associated together by means of hydrogen bonds are formed on the surface of carbon adsorbents and then merge into one another, is a two-dimensional phase transition, and is in many ways analogous to surface condensation; i.e., to a phase change of the first kind.

In the light of the results of the present investigation, the range of relative pressures in which the capillary condensation of water vapor is possible (in pores of active charcoal in the direct sorption process) must be moved to the higher range of relative pressures. The main rise in the sorption isotherm is not associated with capillary condensation, but with the formation of a condensed monomolecular adsorbed layer; i.e., with the stage preceding capillary condensation.

It should be noted that in certain cases, when the active charcoal has a suitable porous structure, the completion of the formation of a condensed adsorbed layer is not expressed by an appreciable inflexion in the sorption isotherm, owing to the superposition of the capillary condensation process.

SUMMARY

1. A detailed study has been made of the sorption isotherms for water vapor on nonporous, thermally-treated carbon black having a known specific surface, and also on a number of samples of active charcoal.

2. It has been shown that, for carbon black and active charcoals, the main rise in the sorption isotherm up to its point of inflexion corresponds to monomolecular adsorption. In the direct sorption process, the region of polymolecular adsorption extends up to high relative pressures, approaching 0.95. For the investigated samples

of active charcoal, the process of capillary condensation does not play an important part.

3. An exposition is given of the concepts developed in our laboratory concerning the mechanism of the sorption of water vapor by carbon adsorbents; it involves the hypothesis of the determining role of hydrogen bonds in the adsorption of water vapor. It is shown that the experimental results are in accord with these concepts.

Received July 17, 1953

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NEW METHOD FOR THE INVESTIGATION OF THE MECHANISM OF CATHODE PROCESSES, AND ITS APPLICATION

M. Smyalovsky and Z. Shklyarskaya-Smyalovskaya

The methods known at present for the investigation of the mechanism and kinetics of electronic processes do not permit us to give an unequivocal explanation of the nature of certain important phenomena accompanying the discharge of ions and separation of gases during electrolysis. This is particularly true of the problem of hydrogen overvoltage, which has long formed an object of investigation and has been the subject of many discussions between the supporters of the theory of slow ion discharge [1] and supporters of other hypotheses, e.g., the adsorption hypothesis [2]. Again, no satisfactory explanation has been found of the penetration of cathodic hydrogen into the inside of a metal, which has been investigated during recent years by, for example, Polukarov [3], Lihl [4], and Glikman and Snezhkova [5].

We have shown in our previous investigations [6] that interesting results, from the point of view of the mechanisms both of cathode processes and of hydrogen diffusion, may be obtained from observations on the extension of a fine wire used as cathode in the electrolysis of aqueous acid and alkaline solutions. The hydrogen atoms that penetrate inside the metal are the source of internal pressures and mechanical stresses, and these result in readily measurable changes in the length of the wire. It was shown that the change in length of a mild steel wire due to hydrogen uptake increased with the degree of recrystallization of the metal during cold working. It was shown by comparative mechanical tests that the value of the extending stresses arising in an iron cathode owing to saturation with hydrogen (in a solution of N sulfuric acid with an addition of thiourea or other substances that retard the recombination of hydrogen atoms to form molecules) probably attains 14 kg/ sq.mm, which corresponds to a pressure of 1400 atm. It must be supposed that no less a pressure will arise at the phase boundary surface between the cathode and the electrolyte. When the solution contains no negative catalysts for the transition $2H \rightleftharpoons H_2$, the pressure will be generated mainly by molecular hydrogen, which cannot penetrate into iron, but in presence of substances that retard the above transition, the length of time during which H atoms exist in contact with the cathode surface will be increased, and this in its turn will result in a high partial pressure of atomic hydrogen, and in the penetration of this gas into the metal. Organic corrosion inhibitors, such as dibenzyl sulfoxide, are adsorbed on the cathode surface. This results in increase in the contact wetting angle at the boundary surface between cathode, electrolyte, and gas, and hence in increase in the size of the gas bubbles [7] and in reduction of the hydrogen pressure at the cathode surface. Such substances, therefore, retard the penetration of hydrogen into the metal.

EXPERIMENTAL

Principle of New Method of Investigating the Diffusion of Cathodic Hydrogen

In the course of studies relating to the deformations of iron cathodes due to hydrogen imbibition, it was found that a fine wire or ribbon bent in the form of the letter C straightens out in the manner of a Bourdon manometer tube as atomic hydrogen penetrates into it. Owing to the creation of high pressures in the internal inter- or intracrystal spaces of the material composing the cathode, forces are produced that tend to increase the radius of curvature of the bent cathode. The effect of these forces can be detected only in the case of objects of small cross-section that are capable of being saturated throughout with hydrogen under certain conditions, and are capable, in the case of annealed metal, of undergoing plastic deformation under the action of small stresses. This effect can be magnified by the use of a cathode made of wire bent in the form of a flat or cylindrical spiral.

Apparatus for measurements of this kind is shown in Fig. 1. The spiral cathode Fe was immersed in N sulfuric acid, and it was loaded at the lower end by the glass weight g, which, in its immersed condition, weighed about 4 g. The initial diameter of the turns of the spiral was 22 mm. In the experiments on the effect of current density and of the concentrations of arsenic and dibenzyl sulfoxide, the number of turns was $t = 14$, the initial length of spiral immersed in the solution was $l_0 = 50$ mm, and the total length of iron wire making up the spiral was $L = 1000$ mm. In the experiments on the effect of various catalyst poisons, the corresponding values were:

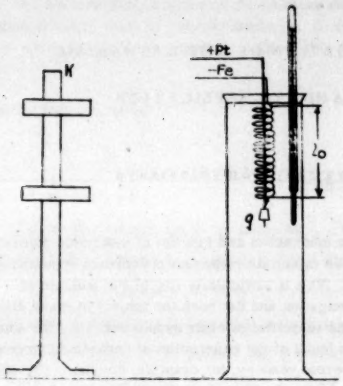

Fig. 1.

t = 7 turns, l_0 = 25 mm, and L = 500 mm. Under the influence of cathodic polarization in presence of substances that retard the recombination of hydrogen atoms to form molecules, the radius of curvature of each turn of iron wire increased somewhat, so that the length of the spiral increased accordingly; the change in length of the spiral was measured with a cathetometer K provided with two reading telescopes.

The anode was either a straight platinum wire, diameter 1 mm, placed along the geometric axis of the iron spiral, as shown in Fig. 1, or a platinum gauze surrounding the spiral. The type of anode used did not affect the results.

Examples of the Application of the New Method

The investigation was carried out on an iron wire, diameter 0.45 mm, and having the following chemical composition (%):

C	Mn	P	S	Cu	Ni
0.09	0.35	0.028	0.048	0.47	0.03

The number of spirals necessary for carrying out a whole series of experiments were prepared, and they were annealed in an atmosphere of hydrogen for 30 minutes at 900° in order to bring about recrystallization, removal of all stresses, and elimination of organic contamination from the surface of the wire. Each spiral was used for one measurement only.

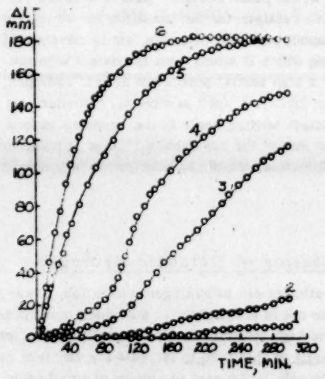

Fig. 2. 1 – 0.0015 mg/liter; 2 – 0.003 mg/liter; 3 – 0.0045 mg/liter; 4 – 0.06 mg/liter; 5 – 3.04 mg/liter; 6 – 30.4 mg/liter.

At the start of the investigations, the effect of temperature in the range 15-50° on the length of the spiral was determined. The spiral was immersed in distilled water, and was not polarized; under these conditions, no effects were observed. Experiment showed that the spiral did not undergo deformation under the influence of cathodic polarization in a solution of pure sulfuric acid; but if electrolysis occurred in the presence of certain elements of Groups V and VI of the periodic system that are known for their tendency to poison contact catalysts, the spiral lengthened rapidly, its movement being frequently observable by the unaided eye, and in some cases it attained a length of more than 1000% of the initial length of the spiral. These effects are irreversible, which is an indication of the plastic nature of the deformation.

The value of the change in length Δl of the spiral due to saturation with cathodic hydrogen must undoubtedly bear a quantitative relation to the value of the internal pressure of the gas accumulated within the structure of the metal; the change in length is established in experiments with satisfactory reproducibility, and hence, on the basis of measurements of the change in the length of the spiral, an idea of the course of the penetration of hydrogen into the metal can be obtained. In Fig. 2 we show the results of observations on the extension of a spiral of t = 14 turns under the conditions required for imbibition of hydrogen at 20° and current density 0.018 amp/sq.cm in N sulfuric acid with additions of As_2O_3 at various concentrations. The time from the beginning of the electrolysis is given in minutes along the axis of abscissas, and the observed lengthening of the spiral is given along the axis of ordinates. Under Fig. 2, concentrations are given; they are expressed as milligrams of arsenic in one liter of acid. As will be seen from the course of these curves, increase in the concen-

tration of arsenic from 0.0015 to 3 mg per liter results in a considerable acceleration of the untwisting of the spiral and the attainment of a high ultimate value of Δl, corresponding to a definite final pressure of hydrogen accumulated within the wire.

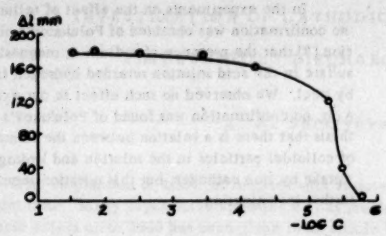

Fig. 3

In Fig. 3 we show the relation of the final value of Δl to the concentration of arsenic, expressed as the negative logarithm of the amount of this element in grams in one liter of the solution; the physical conditions were as before (Fig. 2.). This graph shows that increase in arsenic concentration above a certain limiting value of approximately 0.1 mg per liter produces no further rise in the final value of Δl.

In Fig. 4 we show the relation of the final value of Δl to the current density in milliamperes per sq.cm of the cathode surface, and in Fig. 5, the relation of Δl to the concentration of dibenzyl sulfoxide in grams per one liter of N sulfuric acid. In these experiments a constant arsenic concentration of 1.5 g/liter and a constant temperature of 20° were used. As will be seen from the course of the curve in Fig. 5, dibenzyl sulfoxide at a concentration of 0.03 g/liter completely inhibits the hydrogen-diffusion process, but at higher concentration (above 0.05 g/liter) the inhibiting effect is reduced. This fact can be explained by the decomposition of dibenzyl sulfoxide molecules in the electrolysis. The measurements on the effect of the dibenzyl sulfoxide concentration, the results of which are given in Fig. 5, were carried out at a cathode current density of 0.018 amp/sq.cm. At higher current densities there was a displacement of the minimum of the curve toward higher dibenzyl sulfoxide concentrations.

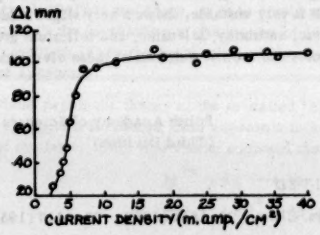

Fig. 4

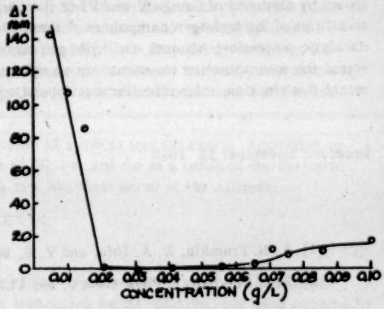

Fig. 5

Particularly interesting results were obtained in a comparison of the effects of various elements of Groups V and VI of the periodic system on the final value of the extension of the spiral (Fig. 6). These measurements were made on spirals for which the number of turns $t = 7$. The cathode current density was 0.036 amp/sq.cm, and the temperature was 20°. The elements examined were Bi, Sb, As, and P (Group V) and Te, Se, and S (Group VI). Bismuth, selenium, tellurium, and antimony were added as oxides, sulfur as hydrogen sulfide, and phosphorus as phosphine. Sulfate and phosphate ions did not promote penetration of hydrogen into an iron cathode. Nitrogen, in the form of NH_4^+ or NO_3^-, also did not induce extension in the spiral cathode.

For all of these elements the dependence of Δl on the concentration was qualitatively similar to that found for arsenic (Fig. 3), but the position of the bend of the curve was different for each element. For all of these elements concentrations of greater than the limiting value were used. In Fig. 6 a comparison is made of the final values of the extension Δl, which are plotted against atomic number. In spite of a certain scatter in the results,

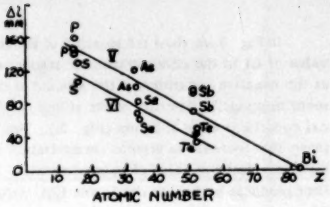

Fig. 6

a definite functional character is evident. Elements of Group V are in general more powerful in their action than those of Group VI, and in each group the activity falls as the atomic weight rises.

In the experiments on the effect of tellurium, no confirmation was obtained of Polukarov's observation [3] that the presence of sodium or magnesium sulfate in the acid solution retarded hydrogen imbibition by steel. We observed no such effect in our experiments. Also, no confirmation was found of Polukarov's hypothesis that there is a relation between the formation of colloidal particles in the solution and hydrogen uptake by iron cathodes, but this question requires further investigation.

SUMMARY

1. The behavior of spirals of iron wire during cathodic polarization indicates the suitability of the described method for the investigation of cathode processes, in particular for the investigation of the effect of the composition of the electrolyte and electrolysis conditions on the form in which hydrogen separates at the cathode.

2. The results of this investigation confirm the conclusions drawn from our previous work, which were that a high hydrogen pressure exists at the surface of a working cathode, the value of which is greatly dependent on the current density and on factors of an electrocapillary nature. In presence of traces of certain Group V and VI elements in the solution, the recombination of hydrogen atoms to form molecules is slowed down so that atomic hydrogen makes an appreciable contribution to the pressure acting on the cathode surface; this in its turn is the cause of the penetration of this gas into the structure of the iron.

3. The varying catalytic effects in the retardation of the recombination of hydrogen atoms into molecules shown by elements of Groups V and VI of the periodic system (Fig. 6) are probably associated with the varying stabilities of the hydrogen compounds of these elements. Nitrogen, which gives the stable compound NH_3, has no catalytic properties; bismuth, the hydrogen compound of which is very unstable, shows a very slight tendency to retard the recombination reaction; but phosphorus, sulfur, arsenic, antimony, selenium, and tellurium greatly retard this reaction, their effectiveness depending on the valencies and atomic numbers of these elements.

Received November 12, 1953

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INVESTIGATION OF CATHODIC POLARIZATION OCCURRING DURING SIMULTANEOUS DISCHARGE OF IRON AND TUNGSTEN IONS

Z. A. Solovyeva and A. T. Vagramyan

The preparation of alloys of tungsten with various metals is a problem of great practical importance at the present time. Many papers have appeared on this problem during recent years. A review and detailed analysis of these papers up to 1940 has been given in an article by Sklyarenko and Druzhinina [1]. The most practical method appears to be the preparation of tungsten from aqueous solutions, and most of the papers, therefore, have been concerned with work in that direction.

The difficulty of preparing tungsten from aqueous solutions is associated with the preferential separation of hydrogen at the cathode owing to the strongly negative potential required for the separation of tungsten and the low value of the hydrogen overvoltage on tungsten. Among the investigations on the preparation of tungsten and its alloys from aqueous solutions, we must draw particular attention to the work of Golts and Kharlamov [2], who, in an investigation in 1936 on the polarization curves obtained in the deposition of tungsten-nickel, demonstrated the lowering of polarization in the deposition of nickel-tungsten, as compared with nickel alone; they showed also that the extent of this lowering increases with rise in temperature, and that this leads to increase in the tungsten content of the deposit.

Further work, by foreign investigators, on the preparation of tungsten alloys developed along the lines indicated by Golts and Kharlamov, namely, increasing of the depolarizing action of the metal codepositing with tungsten by rise in temperature, and addition of ammonium salts to the solution. The investigations on the preparation of tungsten alloys have been directed mainly to the selection of an electrolyte of suitable composition and a satisfactory electrolysis procedure, so as to obtain an alloy of high quality [3]. Very little study, however, has been devoted to the mechanism of the process of depositing electrolytic tungsten alloys. Recently, two papers by Holt and coworkers [4] on the mechanism of simultaneous discharge of ions of tungsten and metals of the iron group have appeared.

In these papers the theory of the so-called "catalytic reduction" of a metal was advanced. According to this theory, tungsten is reduced from aqueous solutions in presence of Ni, Fe, and Co as a result of the catalytic activity of the latter. Holt and Vaaler supposed that the following two reactions occur at the cathode:

$$M^{++} + 2e \longrightarrow M \qquad (1)$$

$$WO_4^{--} + 8H^+ + 6e \longrightarrow W + 4H_2O \qquad (2)$$

Reaction 1 proceeds at the cathode until it is completely covered with a thin deposit of one of the iron-group metals, which encourages the occurrence of Reaction 2. When the iron-group metal (catalyst) has been covered by a layer of tungsten, Reaction 2 ceases and Reaction 1 proceeds again with the formation of a layer of catalyst.

In this way the periodic deposition of layers of iron-group metal (catalyst) and tungsten occurs at the cathode. The grounds for this point of view were found in polarographic investigations and in the investigation of the structure of electrolytic alloys carried out by Brenner, Burkhead, and Seegmiller [5]. In this connection, Holt and Vaaler point out that attempts to measure the potential for the electrodeposition of the alloy by the "direct" method do not give reproducible results. In a recent investigation, Clark and Lietzke showed that tungsten is deposited on a number of metals (Pb, Zn, Cd, Fe, Co, Ni, Cr, W, Cu, Ag, Pt), but the product of the electrochemical reaction is not the pure metal, but tungsten oxide. It was then noted that the largest amount of tungsten was separated in the case of metals of the iron group. The papers cited leave the following questions obscure:

1. Does the separation of tungsten occur as a result of "catalytic" reduction by hydrogen, or does depolarization occur as a result of the formation of a chemical compound or solid solutions between tungsten and the codepositing metal, as in the case of the discharge of sodium ions at a mercury cathode?

2. In the preparation of a tungsten alloy, is the discharge of the codepositing metal held back as a result of complex formation and leveling to the separation potential of tungsten?

For the investigation of alloy deposition we have used a direct method for the measurement of potentials that differs from the usual compensational method in the possibility of recording continuous change of potential of the electrode at any desired rate on photographic film.

EXPERIMENTAL

Method of Measurement

The potential of the electrode was measured with the aid of a high-resistance cathode voltmeter, taking a current of up to 10^{-12} amp, and a short-period mirror galvanometer having a sensitivity of 10^{-6} amp/mm and a period of 0.01 second. Such a method permits potential measurements to be made without the passage of appreciable current.

A 50-cc glass vessel was used as electrolytic cell. The cathode was formed by the end section of a copper or iron wire fused through the glass, the cathode surface being about 0.002 sq.cm; the anode was an iron or tungsten wire. A saturated calomel half-element was used as comparison electrode. The change in the potential of the electrode was recorded by means of the reflected light beam from the galvanometer on photographic film carried by a drum rotating at 1.5 mm per second.

Fig. 1 shows one of the records so obtained; it is a record of the change in the cathodic polarization of an iron electrode with time, the ordinates being potentials in millivolts and the abscissas time in seconds. The plot of the potential on the film was made as follows. A plot was first made of the zero position of the galvanometer, which corresponded to the potential of the calomel half-element to which all values of potential were referred. This line was plotted in a series of separate portions along the whole length of the film (lower, broken line). When the polarization current was switched on, the displacement of the reflection from the galvanometer from the zero line was a measure of the potential φ_1 for the separation of metal. For the determination of the stationary potential φ_0 of the electrode, the polarizing current was switched off after electrolysis had proceeded for a short time, and the position of the reflection from the mirror galvanometer after 15 seconds (sufficient time for the establishment of the potential) could be taken as a measure of φ_0. The deflection of the galvanometer when the current was switched on for a second time corresponded to the potential for the separation on a freshly deposited one-component cathode surface. The overvoltage for the separation of metal is therefore expressed by the difference –

$$\eta = \varphi_1 - \varphi_0 .$$

Experimental Results

In our study of the mechanism of the deposition of alloy, we first studied the cathodic polarization in citric acid solutions containing only iron ions or only tungsten ions, and then studied the simultaneous discharge of these ions. Following Holt, we used solutions containing, per liter, 66 g of citric acid, 50 g of Na_2WO_4, 2 g of Fe^{++} and Fe^{+++}, and NH_4OH to pH 8-8.5.

Cathodic Polarization in the Electrolysis of Solutions Containing Iron Ions. In the investigation of the polarization of iron in citric acid solutions, its dependence on current density, temperature, and the charge of the iron ions was examined. Fig. 2 represents the variation in polarization with time in the electrodeposition of iron from citric acid solution at 25° and at a current density of 5 amp per sq.dm. It will be seen from Fig. 2 that the potential for the separation of iron under these conditions is 1093 mv (section on the left), the stationary potential for iron is 727 mv (middle section), and the overvoltage is 366 mv.

Effect of Temperature. Study of the polarization of an iron electrode has shown that the temperature of electrolysis has a great effect on the polarization and overvoltage during the separation of iron. The results of the investigation are given in Table 1; each experiment was done in duplicate. As will be seen from Table 1, the error in measurement is about 20-30 mv, for the necessity of finding place on 70-80 mm photographic film for a polarization of about 1000 mv makes it impossible to increase the sensitivity of the

TABLE 1

Temperature (°C)	Separation potential (mv)	Stationary potential of iron (mv)	Overvoltage at i = 5 amp/sq.dm, in mv
16	1067; 1095	690; 727	379; 366
70	948; 930	690; 690	253; 241

measurement to more than 15-20 mv per 1-mm deflection of the galvanometer. It will be seen from Table 1 that raising of the temperature facilitates discharge of iron ions to the extent of 80-100 mv.

Effect of Current Density. The effect of current density on the polarization of iron was studied by the rapid method of recording polarization curves. Fig. 3 shows the polarization curve for the iron electrode, and it will be seen that the polarization does not vary linearly with current density. The form of the curve is analogous to the polarization curve for nickel obtained in sulfuric acid solutions [6]. According to the curve, the overvoltage at a current density of i = 5 amp per sq.dm is 374 mv. When the polarization curve is obtained at a different speed, the value of the polarization does not change, thus indicating the absence of concentrational polarization. The broken line in Fig. 3 is the stationary potential of iron at pH 8, which has the value 715 mv. As will be seen from the curve, after a short time the stationary potential is sharply displaced in the positive direction to a value corresponding to the potential of copper, which is the result of the autodissolution of iron in these solutions.

Cathodic Polarization in the Electrolysis of Solutions Containing Tungsten Ions. In the electrolysis of solutions containing only tungsten ions, i.e., in absence of a codepositing metal, no separation of tungsten could be detected, neither by analytical methods, nor by electrochemical methods, such as stationary potential measurements.

Cathodic Polarization in the Electrolysis of Solutions Containing Iron and Tungsten Ions. Study of the polarization in the simultaneous electrodeposition of iron and tungsten has shown that the separation potential for the alloy in citric acid solution at pH 8,1, at room temperature, and at a current density of i = 5 amp/sq.dm is 978 mv, the stationary potential of the alloy is 682 mv, and the overvoltage is 300 mv. The potential for the separation of the iron-tungsten alloy is, therefore, less than that for iron alone by about 120 mv.

It is impossible to compare the potential for the separation of the iron-tungsten alloy with that of pure tungsten, since we have not succeeded in causing the latter to separate from aqueous solutions, but in comparison with the standard potential of tungsten the separation potential for the iron-tungsten alloy (according to thermodynamical calculations) is depressed by 300 mv.

The effect of the electrolysis temperature on the polarization during electrodeposition of the alloy is shown in Table 2, from which it will be seen that raising of the temperature to 70° facilitates the separation of the iron-tungsten alloy to the extent of 100 mv.

TABLE 2

Temperature (°C)	Separation potential at i = 5 amp/sq.dm (mv)	Stationary potential at i = 5 amp/sq.dm (mv)
18	978	632
	978	672
70	879	628
	897	646

TABLE 3

Temperature (°C)	Depression of separation potential of alloy (mv) in comparison with –		$\frac{\Delta \varphi W}{\Delta \varphi Fe}$
	Standard potential of tungsten, $\Delta \varphi W$	Separation potential of iron	
20	320	109	2,9
70	430	208	2,1

It will be seen ffom these results that the separation potential of iron at a current density of i = 5 amp/sq.dm, and at room temperature, is 1087 mv; at 70° it is 930 mv. The separation potential for the alloy, however, is 978 mv at 20° and 879 mv at 70°. The position is made clearer in Table 3, in which the lowering of the separation potential of the alloy with the respect to those of iron and tungsten is shown. It will be seen that the more positive the separation potential of the alloy, the less becomes the relative difference between the separation potentials of iron and tungsten. Rise in temperature, therefore, leads to a positive displacement in the separation potential of the alloy, and so increases the concentration of tungsten in the deposit.

Discussion of Results

In order to obtain an iron-tungsten alloy the separation potentials of the two components must be made to approach one another so that simultaneous deposition is possible. This can be attained in two ways: 1) raise the potential for the separation of the more positive metal (Fe) to that of the tungsten, for example, by complex formation; and 2) lower the separation potential of the more negative metal, for example, by formation of a chemical compound or solid solution.

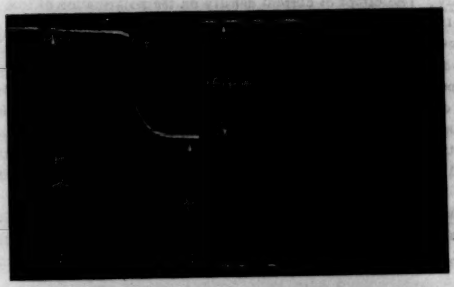

Fig. 1. Change of cathodic polarization with time, before and after switching off the current.

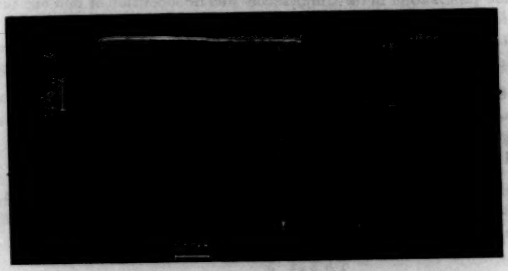

Fig. 2. Change of cathodic polarization with time in the electrodeposition of iron from citric acid solution at 25°C and at a current density of 5 amp/sq. dm.

Fig. 3. Variation of polarization with current density in the electrodeposition of iron (broken line: change in the potential of the electrode with time after switching off the current.)

The first way would not be satisfactory, for at a more negative potential of the electrode in aqueous solutions vigorous separation of hydrogen would occur. The second way is the more expedient, but it must be remembered that the work of formation of the chemical compound must be sufficiently large, in order to make the separation of tungsten possible.

We have already pointed out that, according to Holt and his students, the first stage in the electrodeposition of alloy is the separation of an iron-group metal on the electrode, after which separation of a layer of tungsten occurs on the surface of the catalyst. Holt, unfortunately, does not discuss the mechanism of the catalyzing action of the iron-group metal. In confirmation of his theory, he refers to the photomicrographs of sections taken by Brenner. From the photomicrographs, however, it may be seen that the thickness of individual layers is about 1 μ.

If alternate deposition of tungsten and iron does occur on the cathode, then a periodic variation in the potential should occur, for the potential of the electrode should have a higher value during the separation of an iron-group metal, and then fall by about 100 mv during the separation of the alloy. The period with which the potential would vary would be appreciable, for the deposition of a layer visible on the photomicrographs (X 250) to which Holt refers would require several seconds.

However, as our experiments on the variation of polarization with time have shown, no such variation of potential during electrodeposition of alloy occurs. It is impossible, therefore, to treat the layered structure of the electrolytic deposit that is visible on microsections as the result of the periodic deposition of two metals, all the more since a similar layered structure can be observed in the electrodeposition of a single metal.

It appears more likely that we are concerned here with the same mechanism of deposition as that found in the separation of sodium at a mercury cathode, where as a result of the formation of a chemical compound the potential required for the discharge of a sodium ion is greatly reduced. In the deposition of tungsten alloys, we probably again have the formation of a chemical compound (of the type Fe_2W), and the discharge of tungsten ions is, therefore, greatly facilitated, and the potential required for its separation becomes even less than the standard tungsten potential. The difference lies in the fact that in the electrolytic deposition of tungsten alloys, simultaneous separation of iron and tungsten occurs with formation of an alloy and periodic variation in potential therefore does not occur.

SUMMARY

1. An investigation of the simultaneous deposition of iron and tungsten has shown that the separation potential for the alloy is 100 mv less than the separation potential for iron and 300 mv less than the standard potential of tungsten.

2. It has been shown that the possibility of discharging tungsten ions depends on the depolarizing action of the simultaneous discharge of iron and tungsten ions.

3. It has been shown also that there is no periodic variation in the potential during the electrodeposition of tungsten and iron; which is in conflict with Holt's ideas on the layered deposition of iron and tungsten.

Received May 10, 1953

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REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

COMMUNICATION 2. REACTION OF VITREOUS SODIUM DISILICATE WITH AQUEOUS SOLUTIONS

Yu. A. Shmidt

In the previous paper we described the reaction of vitreous sodium silicates with water and hydrochloric acid solutions [1]. In the present communication we describe a more detailed study of the reaction of vitreous sodium disilicate with various aqueous solutions.

EXPERIMENTAL

We have already described the experimental procedure [1]. For the characterization of the processes occuring, we make use of the following quantities: n_{Na_2O} and n_{SiO_2}, the amounts in moles per sq.cm of the respective oxides passing from the glass into solution; v_{Na_2O} and v_{SiO_2}, the mean rates of the passage of these oxides into solution (mole/sq.cm/min); δ, the thickness of the siliceous film on the surface [1].

In the experiments at 40°, in addition to agitation of the solution with a stirrer, we tried also vigorous shaking (about 1000 shakes per minute) of the sample in the liquid, which aided in the effective removal from the surface of soluble products of the reaction of the glass with the solution. At the beginning of an experiment agitation by shaking resulted in an increase of about 50% in the rate at which Na_2O passed into solution, but later (after one hour) the rate was found to be about the same as that found in the experiments with a stirrer. It may be supposed from this that at the beginning of the experiment an alkaline diffusion layer was formed on the surface of the glass, but later the concentration of alkali at the surface fell and approached the concentration in the solution. More vigorous removal of alkali from the surface by means of shaking led to a reduced value of v_{SiO_2}, the reduction being particularly marked at the beginning of the experiment. In other respects the observed behavior was similar to that observed when agitation was effected with a stirrer.

In order to study the effect of temperature, experiments were carried out at 25°, 55°, 70°, and 100°; the results are given in Table 1. The variation of the values of v_{Na_2O}, v_{SiO_2} and δ with time is shown in Figures 1 and 2. At 25° and 40° the main process is the leaching of the glass, leading to the formation of a residual siliceous film, the thickness of which grows continuously. With rise in temperature the rate of the passage into solution of the components of the glass, particularly silicic acid, rises rapidly, but as the alkali concentration in the solution increases very rapidly in the experiments at 55° and 70°, the thickness of the residual film, having attained a definite limit, begins to decrease. For this reason, the value of v_{Na_2O}, which falls at the beginning of these experiments, then begins to rise. The variation with time of the rate of passage of silicic acid into solution is expressed by curves having maxima that become more marked as the temperature rises, simultaneously moving toward the axis representing the beginning of the experiment.

When vitreous sodium disilicate reacts with water, the concentration of alkali in the solution increases, i.e., there is an increase in the sodium ion concentration, and a reduction in the hydrogen ion concentration. In order to study the effect of variation in the concentration of these ions on the course of the process, experiments were carried out on the reaction of sodium disilicate with 0.01 N, 0.1 N, and N solutions of sodium chloride, and also with 0.01 N solutions of hydrochloric acid and caustic soda. The results of these experiments, which were carried out at 40°, are shown in Figures 3 and 4. With increase in the sodium chloride concentration, and also with decrease in the hydrogen ion concentration, the value of n_{Na_2O} falls somewhat, and that of n_{SiO_2}, on the contrary, rises greatly. Check determinations of the silicic acid in the solution after preliminary heating of it with alkali showed that in all experiments the silicic acid passed into solution in a molecular, or almost molecular, degree of dispersion.

Weighing of the samples before and after the experiment showed that their loss in weight was less than the weight of components found in the solution by analysis. After drying, the surfaces of the samples were covered with cracks. All this points to the presence of water in the surface layer. The calculated amount of water as percent by weight of the silica remaining in the surface layer was about 30. The experiments at 70° and 100° formed an exception: the process occurring amounted to dissolution of sodium disilicate. In this case the loss in weight of the samples coincided with the weight of components found in the solution by analysis, and the dried surfaces of the samples were unchanged in appearance.

In further experiments sodium disilicate powder having a grain size of 140-200 μ was given a full treatment with 0.01 N hydrochloric acid. After being dried in the air at room temperature, it was found to have the following composition: SiO_2 – 81.2%; Na_2O – 0.54%; H_2O – 18.3%. Similar treatment of sodium disilicate filaments, diameter about 100 μ, led to an increase of about 10% in thickness. Hence, in spite of its appreciable water content, the siliceous film formed on the surface of sodium disilicate apparently undergoes very little swelling.

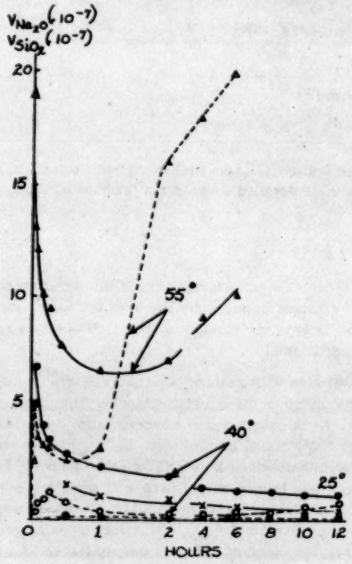

Fig. 1. Variation with time of the rate (mole/sq.cm) of the passage of Na_2O and SiO_2 into solution: ——— v_{Na_2O}; - - - - - - - - - v_{SiO_2}

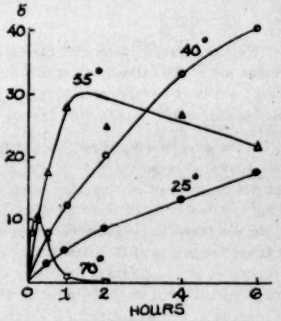

Fig. 2. Variation with time of the thickness of the residual siliceous film δ (in microns) at various temperatures.

Discussion of Results

As indicated in the previous paper, the primary process in the interaction of sodium silicates with water is the exchange reaction between the sodium ions of the glass, and the hydrogen ions in the solution:

$$Na^+_{glass} + H^+_{solution} \rightleftharpoons H^+_{glass} + Na^+_{solution}.$$

It is known from experiment that ion exchange between the surface of a solid (in particular, glass) and a solution proceeds at a high velocity [2, 3, 4]. An equilibrium state is, therefore, reached rapidly, and the ion concentrations in the solid phase at its boundary with the solution are then determined by the composition of the solution, in accordance with the ion-exhcange law [5]. The exchange of ions between glass and solution forms the basis of Nikolsky's theory of the glass electrode [6], which has been confirmed in a number of later investigations [7, 8, 9]. The theory of the glass electrode examines ion exchange at the boundary between glass and solution under equilibrium conditions, and does not concern itself with processes associated with the breakdown of the glass. In the study of the kinetics of the interaction of glass with water, the observed phenomena are more complex, for, in addition to the ion-exchange process, the diffusion of the ions in the solid and liquid phases, and the variation of the thickness of the residual siliceous film with time begin to play a part. When vitreous sodium disilicate inter-

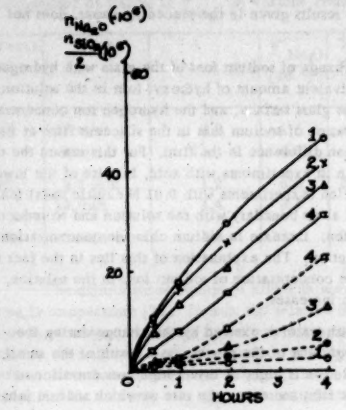

Fig. 3. Interaction of vitreous sodium disilicate with sodium chloride solutions: 1 – water; 2 – 0.01 N NaCl; 3 – 0.1 N NaCl; 4 – 1.0 N NaCl; ——— – n_{Na_2O}; – – – – – – $\frac{n_{SiO_2}}{2}$

Fig. 4. Interaction of vitreous sodium disilicate with solutions of hydrochloric acid and of caustic soda: 1 – 0.01 N HCl; 2 – water; 3 – 0.01 N NaOH; ——— – n_{Na_2O}; – – – – – – $\frac{n_{SiO_2}}{2}$

acts with water, a siliceous film immediately forms on its surface as a result of the exchange of sodium ions of the glass with hydrogen ions of the solution. In this case, therefore, the passage of sodium ions (exchanging with hydrogen ions) from the glass to the solution is made up of a number of processes:

1. Diffusion of Ions in the Siliceous Film. The rate of diffusion is determined by the thickness of the siliceous film, the difference in concentration of sodium ions, and the diffusion coefficient for ions in the film. The last depends on the nature of the exchanging ions and the structure of the film.

2. Passage of Ions from the Surface of the Film to the Solution. On the basis of data available in the literature, it may be supposed that the passage of ions from the surface of the film to the solution proceeds fairly rapidly, in comparison with diffusion processes; as a result, the concentration of ions in the film at its boundary with the solution, if not at the equilibrium value, tends to approach that value.

3. Diffusion of Ions in Solution. The rate of this process depends mainly on the diffusion coefficient for ions in the solution, and the difference in the alkali concentration at the surface and in the solution.

The formation of a siliceous film on the surface retards the passage of sodium ions into the solution to an appreciable extent. This indicates that in this case the slowest stage – the rate-determining stage for the whole process – is the diffusion of ions in the film. The rate of this diffusion depends on the difference of sodium ion concentration within the film. Since the sodium ion concentration at the boundary between unchanged glass and the film is constant, this difference is determined by the value of this concentration at the boundary between the film and the solution. The latter, in its turn, is related to the composition of the solution by the equation of the ion-exchange law:

$$\frac{a_{H^+} \cdot a'_{Na^+}}{a_{Na^+} \cdot a'_{H^+}} = K,$$

(a_{H^+} and a_{Na^+} are the activities of the ions in the solution; a'_{H^+} and a'_{Na^+} are their activities in the siliceous film at its boundary with the solution [6]).

It is known from experiments with a glass electrode that the value of the constant K for glasses that do not contain boric anhydride or aluminum oxide is very small. In an acid medium, therefore, the sodium ion concentration in the film at its boundary with the solution is close to zero, so that the difference in this concentration within

the film has its greatest value and is practically independent of the hydrogen concentration in the solution. As a result, in spite of the great thickness possessed by the film in this case, the rate of passage of sodium ions from glass to solution has its greatest value and, as can be seen from the results given in the preceding paper, does not depend on the concentration of acid.

When vitreous sodium disilicate interacts with water, the exchange of sodium ions of the glass with hydrogen ions of the solution leads to the simultaneous appearance of an equivalent amount of hydroxyl ions in the solution. Immediately, therefore, a layer of alkaline solution is formed at the glass surface, and the hydrogen ion concentration falls to a negligible value. This causes an increase in the concentration of sodium ions in the siliceous film at its boundary with the solution, and so to a reduction in the concentration difference in the film. For this reason the rate of passage of sodium ions from the glass to the solution is lower than in experiments with acid, in spite of the lower thickness of the film. Further increase in the alkalinity of the solution (experiments with 0.01 N caustic soda) lead to still greater increase in the sodium ion concentration in the film at its boundary with the solution and to reduction in the rate of the passage of sodium ions from the glass to the solution. Increase in sodium chloride concentration also reduces the rate of the passage of sodium ions from glass to solution. The explanation of this lies in the fact that, as can be seen from the ion-exchange equation, with increase in the concentration of sodium ions in the solution, their concentration in the film at its boundary with the solution also increases.

An important effect on the interaction of sodium disilicate with water is exerted by the change during the experiment in the thickness of the surface siliceous film. At the beginning of the process, as a result of the small thickness of the film, the rate at which sodium ions pass into the solution is high, so that a high concentration of alkali is immediately formed at the surface. As the thickness of the film increases, the rate at which sodium ions pass into the solution diminishes. At the same time the alkali concentration at the surface is also reduced and approaches the concentration in the bulk of the solution. As, however, the latter concentration increases constantly, the alkali concentration in the solution, interacting with the surface, may again begin to increase as the experiment proceeds further. In a number of cases this increase leads to intensified dissolution of the residual film and to decrease in its thickness, and there is a consequent increase in the rate at which sodium ions pass into the solution.

TABLE 1

Effect of Temperature on the Interaction of Vitreous Sodium Disilicate with Water

Temp. (°C)	Indexes	Time									
		(minutes)						(hours)			
		1	2.5	5	10	15	30	1	2	4	6
25	$n_{Na_2O} \cdot 10^{-6}$	–	–	–	–	–	4.6	7.6	13	20	26
	$n_{SiO_2} \cdot 10^{-6}$	–	–	–	–	–	0.2	0.6	1.2	2.1	2.6
40	$n_{Na_2O} \cdot 10^{-6}$	–	1.7	2.8	4.9	6.6	11	18	30	47	62
	$n_{SiO_2} \cdot 10^{-6}$	–	0.07	0.25	0.66	1.2	2.3	3.2	4.2	5.8	9.3
55	$n_{Na_2O} \cdot 10^{-6}$	1.9	3.9	7.0	12	17	28	48	90	202	317
	$n_{SiO_2} \cdot 10^{-6}$	0.26	1.1	2.0	3.6	5.2	9.2	19	112	328	570
70	$n_{Na_2O} \cdot 10^{-6}$	4.8	11	22	43	64	138	310	643	–	–
	$n_{SiO_2} \cdot 10^{-6}$	5.2	11	23	57	100	256	614	1290	–	–

Note. At 100° the values of n_{Na_2O} and n_{SiO_2} (for one hour) are respectively $3200 \cdot 10^{-6}$ and $6400 \cdot 10^{-6}$ mole/sq.cm.

With rise in temperature the rate at which the components of the glass pass into solution increases considerably. A comparison of values of v_{Na_2O} at various temperatures, but for approximately identical film thicknesses, shows (Table 2) that the rate, and therefore coefficient, of diffusion in the film increases by 7-10% for every degree rise in temperature. Hence, the diffusion coefficient in the film varies with temperature according to a law that is characteristic for solids. This conclusion is in agreement with what we have pointed out above; namely, that the siliceous film on the surface of vitreous sodium disilicate contains 70-80% of SiO_2 and differs little in volume from the original glass.

TABLE 2

Comparison of Values of $\underline{v}_{Na_2O}$ at Various Temperatures

Temp. (°C)	Time	δ (microns)	$\underline{v}^{\circ}_{Na_2O}$ (10^{-7})	Temp. (°C)	Time	δ (microns)	$\underline{v}^{*}_{Na_2O}$ (10^{-7})	$\frac{\underline{v}^{\circ}_{Na_2O}}{\underline{v}^{*}_{Na_2O}}$	Increase in $\underline{v}_{Na_2O}$ (%/1°)
25	30 min	3.3	1.5	40	10 min	3.4	4.2	2.8	7.1
	4 hr	14	0.6		1 hr	13	2.4	4.0	9.8
40	2.5 min	1.2	6.8	55	1 min	1.3	19	2.8	7.1
	15 min	4.4	3.4		5 min	4.4	12	3.5	8.8
55	5 min	4.4	12	70	2.5 min	4.0	41	3.4	8.6

The diffusion coefficient of alkali in solution depends little on the temperature, rising only by 2.4% per degree rise in temperature [10]. Hence, the relative increase in the diffusion coefficient in the film with rise in temperature is considerably greater than the relative increase in this coefficient in the solution, so that the alkali concentration in the solution at the glass surface must increase with rise in temperature. It will not, however, approach saturation. If such saturation were to occur, the slowest stage of the process would be the diffusion of alkali in the solution, and the increase of $\underline{v}_{Na_2O}$ with temperature would be considerably less than that which is observed in practice

These considerations enable us to explain qualitatively the effect of temperature on the interaction of sodium disilicate with water and, in particular, the variation in the form of the maxima on the curves showing the dependence of $\underline{v}_{SiO_2}$ on time at various temperatures. It will be seen from the course of the curves in Fig. 1 that during the first moments of interaction, the rate at which Na_2O passes into solution, and hence the alkali concentration at the surface, is very great. In spite of this, the rate at which silicic acid passes into solution in experiments at 25-55° during the first moments of interaction is zero. This indicates that the dissolution of silicic acid is a considerably slower process and lags behind the transfer to the solution of the corresponding amounts of Na_2O. In the succeeding period the rate at which silicic acid passes into the solution gradually increases. This increase, of course, is the more rapid, the higher the alkali concentration in the surface layer of solution. As we have seen, increase in this concentration is encouraged by rise in temperature.

In the experiments at 25°, the ratio of the diffusion coefficients in the film and in the solution was apparently such that the initial alkali concentration at the surface was relatively low, so that the rate at which silicic acid passed into the solution increased comparatively slowly at the beginning of the experiment and was low in absolute value. The growth in the thickness of the film was also relatively slow. As a result, the reduction in the alkali concentration at the surface proceeded more slowly than in the experiments at higher temperatures. Owing to these circumstances the maximum on the curve of $\underline{v}_{SiO_2}$ against time is attained relatively late and is not strongly marked.

With rise in temperature the initial alkali concentration at the surface increases considerably. At the same time, the rate at which the thickness of the film increases also rises with rise in temperature, leading to a more rapid relative decrease in the alkali concentration at the surface. As a result, the rate at which silicic acid passes into solution at the beginning of the experiment increases at an increasing rate as the temperature rises and attains greater and greater absolute values, though its relative diminution begins more and more early.

The second increase in the rate at which silicic acid passes into solution, which is observed in the experiments at 40-70°, is caused by the increase in concentration of alkali in the main bulk of the solution, which in time overcomes the effect of the reduction in concentration at the surface that occurs at the beginning of the experiment.

With rise in temperature, the rate at which silicic acid passes into solution increases to a considerably greater extent than $\underline{v}_{Na_2O}$. This is to be explained by the sharp increase in the alkali concentration of the solution (both at the surface, and in the body of the solution), and also by the fact that rise in temperature facilitates the breaking of the bonds between the silicon-oxygen groups forming the skeleton of the film. As a result, the leaching of the surface with formation of a siliceous film is replaced as the temperature rises by complete dissolution of this film and hence of the whole of the glass.

The rate at which silicic acid passes into solution depends not only on the temperature, but also on the initial composition of the solution: an increased rate is favored by rise in concentration not only of alkali, but also of sodium chloride In an acid medium, the presence in the solution of an excess of hydrogen ions prevents the formation of alkali at the surface, and for this reason, the amount of silicic acid passing into solution is much less in this case than in the others.

As in the previous investigation, our results suggest that the formation of the siliceous film occurs by the exchange of sodium ions for hydrogen ions in the surface layer of glass. Together with these hydrogen ions, some water penetrates into the surface layer. In all probability, the exchange of sodium ions for hydrogen ions does not result in the breakdown of the bonds present in the glass between the silicon-oxygen tetrahedra, but it undoubtedly has a considerable effect on the state of the surface layer. This is evident from the fact that the same factors that cause an increase (at the expense of hydrogen ions) in the sodium ion concentration in the film at its boundary with the solution also favor the passage of silicic acid into the solution. All our results indicate the dissolution of the siliceous film to be a secondary process occurring by the gradual breaking away of individual silicon-oxygen groups from the surface.

SUMMARY

1. The rate at which sodium ions pass into solution when there is a siliceous film on the surface of vitreous sodium disilicate is determined by the diffusion of the ions in this film.

2. Increase in the sodium ion concentration and decrease in the hydrogen ion concentration of the solution retards the diffusion of sodium ions in the film. At the same time, the rate of the dissolution of the film, which is a secondary process, increases.

3. With increase in temperature, the rate of the diffusion of sodium ions in the film rises greatly. The rate of the dissolution of the siliceous film rises still more, so that with rise in temperature the leaching of the surface of vitreous sodium disilicate is replaced by the complete dissolution of the glass.

Received April 10, 1953

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REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

COMMUNICATION 3. EFFECT OF THE ADDITION OF SILICA AND ALUMINA TO SODIUM SILICATES ON THE INSTABILITY OF THE LATTER TO ACIDS

S. K. Dubrovo

From a study of the nature of the breakdown of silicate glasses under the action of chemical reagents, Grebenshchikov concluded that glass contained a strong silica skeleton, consisting of silica that was not combined with basic oxides [1]. Such a skeleton can be represented as an array of SiO_4 groups (silicon-oxygen tetrahedra) in space. Silicon-oxygen tetrahedra in which the apexes are associated with alkali or alkaline-earth ions form weak, vulnerable links in the skeleton. With increase in the relative number of such groups, the passage of silica into the solution as anions or small aggregates also increases. When alumina is introduced into the composition of vitreous sodium silicates, these glasses undergo radical changes.

As is well known, Vernadsky, in developing the theory of complex siliceous anhydrides and their derivatives, introduced the concept of the identity in the functions of silicon and aluminum in many natural aluminosilicates [2]. This was later confirmed by X-ray analysis for important minerals, such as feldspar, in which it was established that a skeleton built of alternating SiO_4 and AlO_4^- groups was present. In such compounds, therefore, aluminum has a coordination number of four [3]. On the other hand, in some minerals aluminum has a coordination number of six, being a structural analog of magnesium (mica, cyanite, etc.). The variation of the coordination number of aluminum in minerals is reflected in their physical properties [4]. This has served as a basis for the study of the state of aluminum in glasses. A number of investigators have established, with the aid of determinations of refractive index, density, and other physical properties, that in alkaline aluminosilicate glasses aluminum has a coordination number of four and is a structural analog of silicon [5, 6]. In view of these findings, in the study of the interaction of vitreous sodium aluminosilicates with aqueous solutions, it is necessary to pay particular attention to the peculiar features introduced by aluminum when it enters the skeleton of glass.

The aluminum-oxygen tetrahedron AlO_4^- has, in comparison with the silicon-oxygen tetrahedron, an excess negative charge, which is compensated by a sodium ion. This in itself leads to increase in the number of mutually bound silicon-oxygen groups when Al_2O_3 is introduced into the composition of sodium silicates. At the same time there is a reduction in the number of Si–O–Si linkages, owing to the appearance of silicon-oxygen tetrahedra bound at certain apexes to aluminum-oxygen tetrahedra, so that in the skeleton of an aluminosilicate glass depolymerization of silica occurs. It is probable, however, that this depolymerization has a detrimental effect on the strength of the skeleton apparently only in the case of interaction with reagents that selectively leach out aluminum ions; for example, solutions of mineral acids (except hydrofluoric). When a relatively large number of silicon-oxygen groups are bound to aluminum-oxygen groups, then discontinuities will be formed in the skeleton of the glass when the latter are washed out. The residual groups (SiO_4) are isolated, and, being small aggregates, have enhanced solubility in acids. For certain SiO_2/Al_2O_3 ratios in vitreous sodium aluminosilicates, complete dissolution of the glass may occur, no residual layer being formed. In the course of time, depending on the pH of the reacting medium and the concentration of silicic acid in solution, the latter may polymerize, and then coagulate, which is a secondary process. In considering the effect of Al_2O_3 on the properties of vitreous sodium silicates, it is of course necessary to take into account not only the change in the strength of the skeleton of the glass, but also the strength of the electrovalent bonds formed with sodium ions.

In order to obtain a more complete picture of the mechanism of the breakdown of vitreous sodium aluminosilicates under the action of chemical agents, it is desirable to characterize their stability by the individual amounts of the components of the glass passing into the solution. Thus the results of Dimbleby and Turner's experiments [7] on the chemical stability of sodium aluminosilicates are not as valuable as they might be, since the stability is measured by the loss in weight of glass powders when boiled with various reagents, and it is not possible to form an idea of the proportions of the components of the glass passing into solution and so of the extent to which the skeleton of the glass is broken down. Other papers that have appeared in this field are concerned mainly with the more complex sodium calcium aluminosilicates, which we shall not consider here.

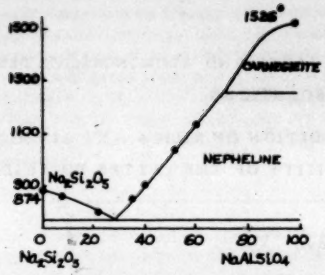

Fig. 1. The sodium disilicate – nepheline section of the phase diagram of the system $Na_2O-Al_2O_3-SiO_2$ (the positions of the investigated aluminosilicates are shown by points).

In sodium aluminosilicates, as in sodium silicates, there first occurs breakdown in the O–Na bond owing to exchange of sodium ions with hydrogen ions of the reacting solution, so that a residual aluminosiliceous layer is formed on the surface of the glass. Aluminum ions are also apparently able to undergo exchange with hydrogen ions.

In the present paper we give the results of an investigation of the course and the character of the breakdown undergone by vitreous sodium aluminosilicates in 0.1 N hydrochloric acid. In the first place, we have studied aluminosilicates whose compositions fall on the disilicate–nepheline section of the phase diagram of the system $Na_2O-Al_2O_3-SiO_2$ (Fig. 1).

EXPERIMENTAL

1. Preparation of Vitreous Sodium Aluminosilicates. For the preparation of aluminosilicate glasses, we used sodium carbonate (pure for analysis), aluminum hydroxide (chemically pure) containing 65.5% Al_2O_3, and ground quartz (containing not more than 0.2% of impurities). The glass was prepared in a platinum crucible at 1400-1500° in a furnace having silit resistors; stirring was performed mechanically with a platinum stirrer. The method of preparing and preserving the samples was the same as in the case of vitreous sodium silicates [8]. The annealing was carefully checked by means of a polariscope. The majority of the investigated glasses were analyzed, and their compositions (according to synthesis and by analysis) are given in Table 1.

TABLE 1

Compositions of the Sodium Aluminosilicates Investigated

Molecular proportions			Composition according to synthesis						Composition by analysis (wt %)			Annealing temp. (°C)
			(mole %)			(wt %)						
Na_2O	Al_2O_3	SiO_2	Na_2O	Al_2O_3	SiO_2	Na_2O	Al_2O_3	SiO_2	Na_2O	Al_2O_3	SiO_2	
1	0.05	2	32.8	1.6	65.6	33.1	2.7	64.2	–	–	–	490
1	0.15	2	31.7	4.8	63.5	31.4	7.8	60.8	–	–	–	510
1	0.30	2	30.3	9.1	60.6	29.2	14.4	56.4	29.2	14.5	56.2	520
1	0.40	2	29.4	11.8	58.8	27.8	18.3	53.9	27.7	18.1	53.7	530
1	0.50	2	28.6	14.3	57.1	26.6	21.9	51.5	26.6	21.7	51.4	540
1	1.0	2	25.0	25.0	50.0	21.8	35.9	42.3	22.3	36.3	41.9	
	Natural nepheline		–	–	–	–	–	–	19.4	34.8	43.3	
	Vitreous nepheline		–	–	–	–	–	–	21.0	34.9	43.4	

2. Procedure. The experiments were carried out in quartz appartus at 40 ± 0.5° in an air thermostat having a bimetal thermoregulator. The method of testing the aluminosilicates was essentially the same as that used for sodium silicates, and we have described this previously [8]. The amounts of the components passing into solution were determined by colorimetric methods. Sodium was separated by means of zinc uranyl acetate, dissolved in acetic acid, and estimated colorimetrically after addition of potassium ferrocyanide (the compound formed by ferrocyanide and potassium uranyl acetate, in amount equivalent to the sodium in the solution, is of a brown color). Silicic acid was determined in solution either as the yellow complex formed with ammonium molybdate, or as molybdenum blue, the reduction product of the yellow complex. The amount of Al_2O_3 in the solution was determined by means of aluminon [9], or, when large amounts were present, the gravimetric hydroxyquinoline method was used also, the method being modified as described by us for the determination of Al_2O_3 in presence of silicic acid [10]. The amounts found by analysis for all of the components of the glass present in the solution were then recalculated as moles of the corresponding oxides passing into the solution per sq.cm of the surface of

the sample, which were denoted respectively as $\underline{n}_{Na_2O}$, $\underline{n}_{Al_2O_3}$ and $\underline{n}_{SiO_2}$.

For the characterization of the interaction of vitreous sodium silicates with aqueous solutions, we have previously made use also of the quantity α, which expresses the fraction of the silicic acid in the reacting layer of glass that passes into solution. In the case of sodium aluminosilicates, we make use of a further analogous quantity β, which expresses the fraction of the alumina present in the attacked layer that passes into solution. Thus, $\beta = \frac{\underline{n}_{Al_2O_3}}{k \cdot \underline{n}_{Na_2O}}$, where $\underline{k}$ is the number of moles of Al_2O_3 entering into the composition of the glass expressed in the form $Na_2O \cdot k\,Al_2O_3 \cdot m SiO_2$. Comparison of the values of α and β gives a clear picture of the mechanism of the breakdown of the glass and the change in the composition of the residual surface layer.

3. Interaction of Sodium Aluminosilicates with 0.1 N Hydrochloric Acid. We have investigated the stabilities of six vitreous sodium aluminosilicates in 0.1 N hydrochloric acid. Each of the investigated samples of aluminosilicates can be regarded in two ways: either as sodium disilicate to which a certain amount of Al_2O_3 has been added, or as a silicate in which part of the SiO_2 has been replaced by Al_2O_3, it being assumed that aluminum is here a structural analog of silicon, when 1 mole of SiO_2 is equivalent to 0.5 mole of Al_2O_3. Hence, when we wish to compare the effects of the contents of SiO_2 and Al_2O_3 in sodium silicates on their stabilities, it is necessary to compare the glasses that can be treated as silicates having additions of SiO_2 and Al_2O_3 in the given proportions.

We have investigated also the action of hydrochloric acid on natural nepheline and on the vitreous product obtained by melting nepheline at 1520°. The nepheline glass was annealed and then sawed into samples with the form of a parallelepiped. In the trials on crystalline and vitreous nepheline and on vitreous sodium aluminosilicate of composition $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$, polished samples were used, whereas the remaining samples had fire-polished surfaces.

Natural nepheline does not belong quite strictly to the sodium disilicate series, for it contains rather too much silica and about 0.6% of extraneous materials. The molecular proportions of the oxides present are, however, found by analysis to be close to those of an aluminosilicate of composition $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$, so that we considered it desirable to determine its stability under the same conditions. Also, it was considered to be of interest to compare the stabilities of vitreous and crystalline samples having the same composition, as we have previously done in the case of feldspars [11].

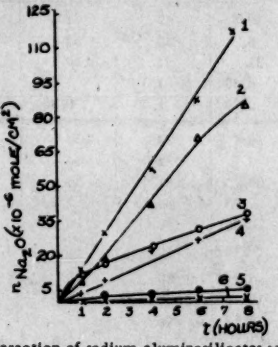

Fig. 2. Interaction of sodium aluminosilicates with 0.1 N hydrochloric acid at 40°: 1 – $Na_2O \cdot 0.4\,Al_2O_3 \cdot 2SiO_2$; 2 – $Na_2O \cdot 0.5Al_2O_3 \cdot 2SiO_2$; 3 – $Na_2O \cdot 0.05Al_2O_3 \cdot 2SiO_2$; 4 – nepheline glass; 5 – $Na_2O \cdot 0.15Al_2O_3 \cdot 2SiO_2$; 6 – $Na_2O \cdot 0.3Al_2O_3 \cdot 2SiO_2$.

The results of the interaction of the investigated sodium aluminosilicates with 0.1 N hydrochloric acid are given in Table 2 and Fig. 2. The first addition of Al_2O_3 (0.05 mole, i.e., 1.6 mole %) immediately produced a sharp fall in the amount of Na_2O passing into the solution (as compared with the disilicate itself). After an eight-hour treatment of disilicate with 0.1 N hydrochloric acid, $\underline{n}_{Na_2O}$ was 109, whereas the corresponding value for the aluminosilicate $Na_2O \cdot 0.05Al_2O_3 \cdot 2SiO_2$ was 38. The value of α for this aluminosilicate was also less than for the disilicate, although the amount of SiO_2 passing into solution was extremely small in both cases and lagged greatly behind the amount of Na_2O in the solution.

As will be seen from Table 2, the succeeding additions of Al_2O_3 to disilicate in the quantities of 0.15 and 0.3 mole led to still further reductions in the value of $\underline{n}_{Na_2O}$. At the same time, some increase in the values of α and β was observed, which was evidence of the incipient breakdown of the aluminosiliceous skeleton of the glass, from which aluminum ions pass preferentially into the solution (β greater than α). The residual protective layer, therefore, was enriched in silica. From a glass of composition $Na_2O \cdot 0.3Al_2O_3 \cdot 2SiO_2$, treated with 0.1 N hydrochloric acid for eight hours, aluminum oxide was leached out to the extent of 60% of its content in the residual layer, whereas only 6% ($\alpha = 0.06$) of the silica was leached out.

When the amount of Al_2O_3 added to sodium disilicate was increased to 0.4 mole, the glass underwent intensive breakdown: for all of the components, the amount passing into solution was greatly increased, aluminum ions being

TABLE 2

Interaction of Sodium Aluminosilicates with 0.1 N Hydrochloric Acid at 40°

Molecular proportions			Mole sq.cm $\cdot 10^{-6}$	Time (hours)				
Na_2O	Al_2O_3	SiO_2		1	2	4	6	8
1	0.05	2	$\underline{n}Na_2O$	12	17	24	32	38
			$\underline{n}Al_2O_3$	–	–	0.01	0.01	0.01
			$\underline{n}SiO_2$	–	–	0.007	0.02	0.02
			β	–	–	0.009	0.006	0.006
			α	–	–	0.0002	0.0003	0.0003
1	0.15	2	$\underline{n}Na_2O$	0.85	2.5	3.0	4.2	4.9
			$\underline{n}Al_2O_3$	–	–	0.006	0.03	0.02
			$\underline{n}SiO_2$	–	–	0.006	0.008	0.02
			β	–	–	0.013	0.05	0.03
			α	–	–	0.001	0.001	0.002
1	0.3	2	$\underline{n}Na_2O$	0.6	1.1	1.2	1.6	2.0
			$\underline{n}Al_2O_3$	–	–	0.36	0.34	0.36
			$\underline{n}SiO_2$	–	–	0.15	0.17	0.22
			β	–	–	1.0	0.71	0.60
			α	–	–	0.06	0.05	0.05
1	0.4	2	$\underline{n}Na_2O$	14	30	58	88	117
			$\underline{n}Al_2O_3$	6.0	13.0	25	35	48
			$\underline{n}SiO_2$	15	31	64	102	109
			β	1.05	1.07	1.06	1.0	1.02
			α	0.55	0.51	0.56	0.58	0.55
1	0.5	2	$\underline{n}Na_2O$	9	19	42	71	86
			$\underline{n}Al_2O_3$	4.4	8.7	20	32	41
			$\underline{n}SiO_2$	20	31	91	136	176
			β	0.91	0.90	1.0	0.90	0.96
			α	1.06	0.90	1.08	0.95	1.03
1	1	2	$\underline{n}Na_2O$	5.3	10.4	23.0	34	47
			$\underline{n}Al_2O_3$	4.7	9.7	22.0	34	46
			$\underline{n}SiO_2$	10	20	41.0	66	91
			β	0.90	0.93	0.95	1.0	0.98
			α	0.94	0.96	0.90	0.96	0.97
Vitreous nepheline								
1	1.04	2.17	$\underline{n}Na_2O$	4.0	8.6	20	35	47
			$\underline{n}Al_2O_3$	4.5	10.2	23	37	49
			$\underline{n}SiO_2$	11	24	45	71	106
			β	1.08	1.1	1.1	1.0	1.0
			α	1.1	1.2	1.04	1.07	1.03
Natural crystalline nepheline			$\underline{n}Na_2O$	27	53	79	74	72
			$\underline{n}Al_2O$	35	66	91	96	96
			$\underline{n}SiO_2$	76.0	140	177	179	149

completely washed out of the layer attacked and SiO_2 being removed to the extent of about 55%. As a result of the action of 0.1 N hydrochloric acid on glass of this composition, a weak spongy residual layer of almost pure silicic acid was formed on the surface. Further increase in the amount of Al_2O_3 added to sodium disilicate resulted in an increase in the amount of SiO_2 passing into the solution from the glass, and the aluminosilicate $Na_2O \cdot 0.5Al_2O_3 \cdot 2SiO_2$, when treated with hydrochloric acid, behaved in such a way that the proportions of the oxides passing into solution corresponded to the proportions existing in the glass before its treatment with acid:

the glass practically dissolved, and the values of α and β approximated to unity. A similar behavior was found for a glass corresponding in composition to sodium disilicate with the addition of one mole of Al_2O_3, when treated with 0,1 N hydrochloric acid.

As will be seen from Table 2 and Fig. 2, the values of n_{Na_2O} fall as we pass to compositions having an Al_2O_3 addition of more than 0,4 mole. The rate of the breakdown of vitreous nepheline prepared by fusing the natural product is the same as that of the aluminosilicate having the oxide proportions of 1:1:2. Natural crystalline nepheline is broken down by 0,1 N hydrochloric acid appreciably more rapidly than the vitreous form, a fact that is probably to be explained by the greater possibility for the solution to penetrate into the sample owing to the presence of cleavage planes.

TABLE 3

Comparison of the Instabilities of Sodium Silicates and Aluminosilicates in 0,1 N HCl (40°, 8 hours)

Indexes	$Na_2O \cdot 2SiO_2$	Moles of SiO_2 added to the disilicate				Moles of Al_2O_3 added to the disilicate					
		0.3	0.6	1.0	2.0	0.05	0.15	0.3	0.4	0.5	1.0
$n_{Na_2O} \cdot 10^{-6}$	109	57	28	10	1.7	38	4.9	2.0	117	86	47
$n_{SiO_2} \cdot 10^{-6}$	0.3	0	0	0	0	0.02	0.02	0.22	109	176	91
$n_{Al_2O_3} \cdot 10^{-6}$	–	–	–	–	–	0.01	0.02	0.36	48	41	46
α	0.001	0	0	0	0	0.0003	0.002	0.06	0.55	1.03	0.97
β	–	–	–	–	–	0.006	0.03	0.6	1.02	0.96	0.98
δ	80	46	25	10	2.2	29	3.9	1.6	105	80	53

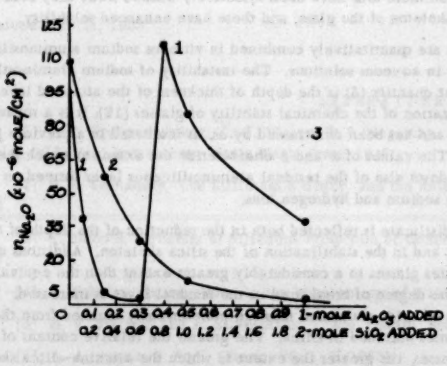

Fig. 3. Comparison of the instabilities of silicates and of the equivalent aluminosilicates in 0.1 N hydrochloric acid; 1) sodium aluminosilicates; 2) sodium silicates; 3) natural nepheline

In Table 3 and Fig. 3 results are given that indicate the comparative stabilities of sodium silicates and the corresponding aluminosilicates to 0.1 N hydrochloric acid. It will be seen that we regard each of the investigated glasses as disilicate having an addition of a certain number of moles of SiO_2 or Al_2O_3. By the use of such a method of representation, it is possible to make a very precise comparison of the relative effects of the presence of SiO_2 and Al_2O_3 in sodium silicates on their instabilities in aqueous solutions. The value of δ given in Table 3 characterizes the depth of the attacked layer or, what amounts to the same, its thickness; it is calculated by the formula that we cited in a previous paper [8].

The results cited indicate that small additions of Al_2O_3 to sodium disilicate are much more effective in reducing instability than equivalent additions of SiO_2. Thus, an addition of 0.3 mole of SiO_2 produces a reduction in the depth of the attacked layer of disilicate by a factor of 1.7, whereas the equivalent addition of 0.15 mole of Al_2O_3 reduces it by a factor of 20. Further additions of Al_2O_3 increase the depth of the attacked layer up to a certain limit.

On the curve in Fig. 3 that expresses the relation between the amount of Na_2O passing into the solution and the amount of Al_2O_3 added to the disilicate, there is a maximum in the region of the composition $Na_2O \cdot 0.4\ Al_2O_3 \cdot 2\ SiO_2$. This composition, however, does not correspond to any particular point on the phase diagram of $Na_2O - Al_2O_3 - SiO_2$.

With increase in the addition of SiO_2 to sodium disilicate, the instability of the resulting silicate falls continuously. The residual siliceous layer on the surface of sodium silicates does not undergo further destruction, and for all of the investigated silicates, apart from the disilicate, the value of α remains equal to zero. In the case of

aluminosilicates, however, α rises continuously as the aluminum content increases, and for the aluminosilicate having oxide proportions of 1:0.5:2, $\alpha = 1$. This difference in the behavior of additions of Al_2O_3 and SiO_2 with respect to the nature and degree of the breakdown of sodium silicates can be explained from the point of view of redistribution of bonds in the glass resulting from these additions.

DISCUSSION OF RESULTS

In sodium disilicate, on the average three apexes of each silicon-oxygen tetrahedron are bound to neighboring tetrahedra, and only one apex is bound to sodium. When a certain amount of SiO_2 is added to disilicate, silicon-oxygen groups that are attached to one another at all apexes appear. The number of such groups increases with increase in the amount of SiO_2 added, and this increases the stability of the skeleton with respect to the action of acid solutions.

When Al_2O_3 is added to disilicate, then as indicated above there is on the one hand an increase in the number of Si−O−Si linkages owing to the fact that the aluminum-oxygen tetrahedron with its excess negative charge is able to retain a sodium ion in its neighborhood, and, on the other hand, the number of silicon-oxygen groups linked together is greatly reduced, because every aluminum-oxygen tetrahedron can bind four silicon-oxygen groups.

The following types of bonds, which apparently differ energetically among themselves, can be considered to be present in vitreous sodium aluminosilicates: 1) Si−O−Si, all of the apexes of the silicon-oxygen tetrahedra being directly attached to one another; 2) Si−O−Al or Si−O−Na, the remaining three apexes being attached to silicon; 3) Al−O−Si−O−Al or Na−O−Si−O−Al, only two apexes of the silicon oxygen tetrahedron being attached to silicon; 4) silicon-oxygen groups, three apexes being attached to sodium and aluminum, and one apex with silicon; 5) silicon-oxygen tetrahedra in which all apexes are attached to sodium and aluminum. It will be clear that O−Al bonds are not equivalent to O−Na bonds, but they are here included conventionally in one group in order to characterize the degree of depolymerization of silica in glass. The weakest bonds with respect to resistance to the action of acid solutions will be those of Types 4 and 5, for when aluminum ions have been selectively washed away they lead to the formation of isolated silicon-oxygen groups in the skeleton of the glass, and these have enhanced solubility.

The way in which the above types of bond are quantitatively combined in vitreous sodium aluminosilicates determines the degree of instability of the latter in aqueous solutions. The instability of sodium aluminosilicates can be characterized by two quantities. The first quantity (δ) is the depth of thickness of the attacked layer and was introduced by Grebenshchikov for the characterization of the chemical stability of glasses [12]; it is a measure of the breakdown of the electrovalent bond O−Na, and has been determined by us, as indicated in a previous paper [8], from the amount of Na_2O passing into solution. The values of α and β characterize the extent to which the skeleton of the glass is broken down, and hence the breakdown also of the residual aluminosiliceous layer formed on the surface of the glass as a result of exchange between sodium and hydrogen ions.

The effect of additions of SiO_2 to sodium disilicate is reflected both in the reduction of the depth of the layer of glass disrupted by the action of acid solutions, and in the stabilization of the silica skeleton. Additions of Al_2O_3 reduce the degree of breakdown of aluminosilicates glasses to a considerably greater extent than the equivalent additions of SiO_2. At the same time, however, the degree of breakdown in the residual layer is increased. This breakdown proceeds as follows: under the action of acids aluminum ions are preferentially leached from the alumina-silica skeleton, and the surface of the glass becomes enriched in silica. The greater the relative content of Al_2O_3, in comparison with SiO_2, in soda-alumina-silica glasses, the greater the extent to which the alumina-silica skeleton is weakened with respect to attack by acids.

As pointed out above, increase in the amount of Al_2O_3 added to sodium disilicate results in increase in the number of sodium ions required to compensate for the negative charges of the aluminum-oxygen tetrahedra. Thus, for an aluminosilicate of composition $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$, all of the sodium ions may be associated with aluminum-oxygen tetrahedra. This type of binding of sodium ions is apparently stronger than the Si−O−Na binding. This is probably the explanation of the slower breakdown of nepheline glass, as compared with that of a glass having an addition of 0.5 mole of Al_2O_3, although the nature of the breakdown is the same in both cases.

The notable fall in the amount of Na_2O passing into solution observed when small amounts of Al_2O_3 are added to disilicate cannot be explained solely by the attachment of sodium ions to aluminum-oxygen tetrahedra. Here we must probably take into account the stabilizing effect of aluminum ions on the Si−O−Na linkage.

On the basis of all these considerations, we may form the following picture of the processes occurring when sodium aluminosilicates interact with solutions of acids. The primary process, as in the case of sodium silicates, is the exchange of sodium ions attached through oxygen to silicon with hydrogen ions from the solution. Later, exchange occurs also between aluminum and hydrogen ions, and this second reaction apparently occurs more slowly.

Together with the passage of aluminum ions into the solution, transfer must occur also of the sodium ions associated with the aluminum-oxygen tetrahedra. This, in fact, may be the explanation of the sharp increase in the amount of Na_2O passing into solution over a comparatively narrow range of compositions (Fig. 3). When aluminum ions have been washed from the skeleton, isolated silicon-oxygen groups, or small aggregates of these, begin to pass into the solution. The exchange between aluminum ions in the glass and hydrogen ions is apparently more dependent on the hydrogen ion concentration than the exchange between sodium ions and hydrogen ions.

SUMMARY

1. The chemical stability of vitreous sodium aluminosilicates can be characterized by the depth of the attacked layer of glass (δ), which is a measure of the breakdown of electrovalent O—Na bonds, and by the degree of breakdown suffered by the aluminum-silicon-oxygen of the glass, expressed by the proportions of the Al_2O_3 and SiO_2 originally present in the residual surface layer that have passed into the solution.

2. With increased additions of SiO_2 to sodium silicates, the depth of the attacked layer of glass falls and the silica skeleton is strengthened.

3. When alumina is introduced into sodium silicates, on the one hand there is an increase in the number of silicon-oxygen groups that become united owing to the neutralization by sodium ions of the extra negative charge of the aluminum-oxygen tetrahedra, and on the other hand, owing to the formation of Si—O—Al linkages, depolymerization of silica in the glass increases, with the result that the instability of aluminosilicate glasses in acid solutions increases greatly when the amount of aluminum oxide added to sodium disilicate exceeds 0.3 mole.

4. The mechanism of the interaction of sodium aluminosilicates with solutions of acids may be regarded as the combination of processes of ion exchange between sodium and aluminum in the glass and hydrogen in the solution, followed by the passage into the solution of small isolated aggregates of silicon-oxygen groups.

Received May 16, 1953

Institute of Silicate Chemistry of the
USSR Academy of Sciences

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SYNTHESIS OF SULFUR-CONTAINING POLYHALO COMPOUNDS AND OF ω,ω'-THIODICARBOXYLIC ACIDS

A. N. Nesmeyanov, L. I. Zakharkin, and R. G. Petrova

The accessibility of tetrachloroalkanes of structure $CCl_3-CH_2-(CH_2)_n Cl$ [1] (n = 1, 3, 5, 7), and of the trichloroalkenes $CCl_2=CH-(CH_2)_nCl$ [2] and ω-chloro carboxylic acids [3] that are readily prepared from them, permits the synthesis of a number of sulfur derivatives containing trichloromethyl, dichlorovinyl, or carboxyl groups. We know only of three very short communications relating to the synthesis of sulfides containing trichloromethyl or dichlorovinyl groups and having more than two carbon atoms in the radical and to the synthesis of ω,ω'-thio dicarboxylic acids having more than four carbons in the radical.

Thus, in a patent [4] reference is made to the preparation of 5,5'-thiodivaleric acid by the hydrolysis of bis(5,5,5-trichloropentyl) sulfide, but neither the reaction conditions nor the proportions of reactants are given, and none of the properties of bis(5,5,5-trichloropentyl) sulfide are described. In another patent [5] there is a description of the preparation of 5,5'-sulfonyldivaleric acid from 1,4-dichlorobutane. A brief indication of the method of preparation of 5,5'-thiodivaleric acid from 5-bromovaleric acid has also appeared [6].

In the present paper we describe sulfides that we have prepared in the following ways:

$$CCl_3-CH_2-(CH_2)_nCl \xrightarrow{Na_2S} [CCl_3-CH_2-(CH_2)_n]_2S,\ n = 3.$$

$$CCl_2=CH-(CH_2)_nCl \xrightarrow{Na_2S} [CCl_2=CH-(CH_2)_n]_2S,\ n = 1,\ 3,\ 5.$$

$$HO_2C-CH_2-(CH_2)_nCl \xrightarrow{Na_2S} [HO_2C-CH_2-(CH_2)_n]_2S,\ n = 5,\ 7.$$

By the action of sodium sulfide on 1,1,3-trichloropropene, on 1,1,5-trichloro-1-pentene, and on 1,1,7-trichloro-1-heptene we have obtained good yields of bis(3,3-dichloroallyl) sulfide, bis(5,5-dichloro-4-pentenyl) sulfide, and bis(7,7-dichloro-6-heptenyl) sulfide. Reaction was fairly rapid, and was complete in three hours. Similarly, more prolonged heating of 1,1,1,5-tetrachloropentane with sodium sulfide gave bis(5,5,5-trichloropentyl) sulfide in a yield of more than 80%, a small amount of the dehydrochlorinated sulfide being obtained as by-product. In the case of the reaction of 1,1,1,3-tetrachloropropane with sodium sulfide, dehydrochlorination was the main reaction, and it was not found possible to obtain bis(3,3,3-trichloropropyl) sulfide. The chlorine-containing sulfides obtained were quite stable compounds, distillable without decomposition under reduced pressure.

7,7'-Thiodiheptanoic acid and 9,9'-thiodinonanoic acid were obtained in good yield by the action of sodium sulfide on the salts of the corresponding chloro carboxylic acids in aqueous solution. From these acids, the ethyl and butyl esters were prepared in the usual way. The esters of 7,7'-thiodiheptanoic acid are liquids, distillable without decomposition under reduced pressure; the esters of 9,9'-thiodinonanoic acid are low-melting solids.

The sulfides obtained, which contained trichloromethyl, dichlorovinyl, and carboxyl groups, were oxidized to sulfoxides and sulfones. A solution of hydrogen peroxide in glacial acetic acid was used as oxidizing agent. Bis(5,5,5-trichloropentyl) sulfoxide is a crystalline solid, and the sulfoxides containing dichlorovinyl groups are thick oils, which do not crystallize after long standing. Some of the sulfones that we have prepared are substances that readily cyrstallize and have sharp melting points.

When bis(3,3-dichloroallyl) sulfone is treated with chlorine in chloroform solution, with irradiation and application of heat, two atoms of chlorine are taken up, and a crystalline product of m.p. 187-188° is obtained; it was not investigated in detail.

EXPERIMENTAL

Bis(3,3-dichloroallyl) Sulfide $[CCl_2=CH-CH_2]_2S$

A mixture of 40 g of 1,1,3-trichloropropene, an aqueous solution of 34 g of sodium sulfide ($Na_2S \cdot 9H_2O$), and 100 ml of ethanol was boiled under stirring for three hours. The alcohol was distilled off, and the residue was poured into water and extracted with chloroform. The chloroform was distilled off, and the residue was vacuum-distilled,

yielding 27.8 g (80%) of bis(3,3-dichloroallyl) sulfide, b.p. 92-94° at 1 mm, n_D^{25} 1.5630; d_4^{25} 1.4451; found MR 56.55; calculated MR 56.44.

Found %: C 28.67; 28.58; H 2.39; 2.50
$C_6H_6Cl_4S$. Calculated %: C 28.57; H 2.37

Oxidation of bis(3,3-dichloroallyl) sulfide with a solution of 30% hydrogen peroxide in glacial acetic acid yielded bis(3,3-dichloroallyl) sulfone, m.p. 114-115° (from alcohol).

Found %: C 25.60; 25.54; H 2.11; 1.91
$C_6H_6Cl_4O_2S$. Calculated %: C 25.35; H 2.11

Addition of Chlorine to Bis(3,3-dichloroallyl) Sulfone

A solution of 5 g of the sulfone in 30 ml of chloroform was illuminated and heated, and chlorine was passed for two hours. The chloroform was then distilled off, and the residue was recrystallized from a large amount of ethanol, yielding 2.7 g of substance, m.p. 187-188°.

Found %: C 20.46; 20.53; H 1.99; 1.78
$C_6H_6Cl_8O_2S$. Calculated %: C 20.31; H 1.72

Bis(5,5-dichloro-4-pentenyl) Sulfide $[CCl_2{=}CH{-}(CH_2)_2]_2S$

From 40 g of 1,1,5-trichloro-1-pentene, 28 g of sodium sulfide, 12 ml of water, and 80 ml of ethanol, the procedure described above yielded 27 g (75%) of bis(5,5-dichloro-4-pentenyl)sulfide, b.p. 147° (1 mm); n_D^{25} 1.5368; d_4^{25} 1.2818; found MR 74.92; calculated MR 74.91.

Found %: C 39.31; 39.34; H 4.57; 4.64
$C_{10}H_{14}Cl_4S$. Calculated %: C 38.96; H 4.54

Oxidation of bis(5,5-dichloro-4-pentenyl) sulfide with a solution of 30% hydrogen peroxide in glacial acetic acid yielded the sulfone, which was an oil that could not be vacuum-distilled without decomposition.

Bis(7,7-dichloro-6-heptenyl) Sulfide $[CCl_2{=}CH{-}(CH_2)_4]_2S$

From 20 g of 1,1,7-trichloro-1-heptene, 12 g of sodium sulfide ($Na_2S \cdot 9H_2O$) in 10 ml of water, and 60 ml of ethanol, the procedure described above yielded 14.1 g (78%) of bis(7,7-dichloro-6-heptenyl) sulfide, b.p. 186-187° (1.5 mm); n_D^{25} 1.5214; d_4^{25} 1.1853; found MR 93.57; calculated MR 93.39.

Found %: C 45.96; 46.27; H 6.22; 6.09
$C_{14}H_{22}Cl_4S$. Calculated %: C 46.15; H 6.04

Oxidation of bis(7,7-dichloro-6-heptenyl) sulfide with a solution of 30% hydrogen peroxide in glacial acetic acid yielded the sulfone as an oil that could not be vacuum-distilled without decomposition.

Bis(5,5,5-trichloropentyl) Sulfide $[CCl_3{-}CH_2{-}(CH_2)_2]_2S$

A vigorously stirred mixture of 105 g of 1,1,1,5-tetrachloropentane, a solution of 60 g of sodium sulfide ($Na_2S \cdot 9H_2O$) in 30 ml of water, and 150 ml of ethanol was boiled for eight hours. The alcohol was distilled off, and the residue was poured into water and extracted with chloroform. The chloroform extract was dried with calcium chloride, the chloroform was distilled off, and the residue was vacuum-distilled, yielding 82.5 g of a fraction boiling at 203-205° at 5 mm. This substance crystallized out almost completely when cooled. A small amount of oil was removed by filtration, and the crystals were washed several times with methanol; m.p. 35-36° (from alcohol).

Found %: C 31.64; 31.68; H 4.29; 4.36; S 8.30; 8.33
$C_{10}H_{16}Cl_6S$. Calculated %: C 31.49; H 4.19; S 8.38

Analysis of the noncrystallizing oil showed that it consisted of a mixture of partially dehydrochlorinated products, which gave 5,5'-thiodivaleric acid when hydrolyzed with concentrated sulfuric acid.

Oxidation of 10 g of bis(5,5,5-trichloropentyl) sulfide with 3.3 g of 27% hydrogen peroxide in 25 ml of glacial acetic acid yielded bis(5,5,5-trichloropentyl) sulfoxide, m.p. 67-68° (from petroleum ether).

Found %: C 30.63; 30.81; H 4.04; 4.28; S 7.92; 7.84
$C_{10}H_{16}Cl_6OS$. Calculated %: C 30.23; H 4.03; S 8.06

Oxidation of bis(5,5,5-trichloropentyl) sulfide with excess of a solution of 30% hydrogen peroxide in glacial acetic acid yielded bis(5,5,5-trichloropentyl) sulfone, m.p. 114-115° (from alcohol).

Found %: C 29.40; 29.39; H 4.10; 4.02; S 7.59; 7.51

$C_{18}H_{28}Cl_6O_2S$. Calculated %: C 29.05; H 3.87; S 7.74

7,7'-Thiodiheptanoic Acid $[CO_2H-(CH_2)_6]_2S$

The sodium salt of 7-chloroheptanoic acid was prepared from 34 g of 7-chloroheptanoic acid and 8 g of caustic soda in 100 ml of water, and to the solution obtained 25 g of sodium sulfide ($Na_2S \cdot 9H_2O$) was added. The mixture was heated under reflux for two hours. The cooled solution was filtered, and the filtrate was acidified with concentrated hydrochloric acid. The white precipitate of 7,7'-thiodiheptanoic acid was filtered off, washed with cold water, and dried. The yield was 26.8 g (89.5%); m.p. 96-97° (from dilute alcohol).

Found %: C 58.23; 57.93; H 8.87; 9.12; S 10.62; 10.57

$C_{14}H_{26}O_4S$. Calculated %: C 57.95; H 9.00; S 11.03

The sulfone was prepared by oxidation of the sulfide with excess of a solution of 30% hydrogen peroxide in glacial acetic acid; m.p. 156-157° (from alcohol).

Found %: C 52.26; 52.22; H 8.07; 8.18

$C_{14}H_{26}O_6S$. Calculated %: C 52.17; H 8.07

The diethyl ester of 7,7'-thiodiheptanoic acid had the following constants: b.p. 183-184° (1.5 mm); n_D^{20} 1.4660; d_4^{20} 0.9951; found MR 96.64; calculated MR 96.48.

Found %: C 62.65; 62.53; H 9.57; 9.64; S 9.38

$C_{18}H_{34}O_4S$. Calculated %: C 62.42; H 9.82; S 9.22

The dibutyl ester of 7,7'-thiodiheptanoic acid had the following constants: b.p. 214-215° (1.5 mm); n_D^{20} 1.4641; d_4^{20} 0.9678; found MR 114.91; calculated MR 115.11.

Found %: C 65.67; 65.61; H 9.89; 9.87; S 8.18; 8.06

$C_{22}H_{42}O_4S$. Calculated %: C 65.67; H 10.44; S 7.97

9,9'-Thiodinonanoic Acid $[CO_2H-(CH_2)_8]_2S$

A solution of the sodium salt of 9-chlorononanoic acid prepared from 27 g of 9-chlorononanoic acid and 5.7 g of caustic soda in 100 ml of water was heated with 17 g of sodium sulfide for three hours, and yielded 22.4 g (92%) of 9,9'-thiodinonanoic acid, m.p. 98-99° (from alcohol).

Found %: C 62.40; 62.58; H 10.28; 10.05; S 9.50; 9.24

$C_{18}H_{34}O_4S$. Calculated %: C 62.42; H 9.82; S 9.22

The sulfonyldinonanoic acid was obtained by oxidation of the sulfide with excess of a solution of 30% hydrogen peroxide in glacial acetic acid; m.p. 148-149° (from alcohol).

Found %: C 56.83; 56.74; H 9.03; 9.03; S 8.67; 8.56

$C_{18}H_{34}O_6S$. Calculated %: C 57.12; H 9.00; S 8.46

The diethyl ester of 9,9'-thiodinonanoic acid had b.p. 219-220° (2 mm); m.p. 37-38° (from petroleum ether).

Found %: C 66.19; 65.91; H 10.46; 10.47

$C_{22}H_{42}O_4S$. Calculated %: C 65.65; H 10.44

The dibutyl ester of 9,9'-thiodinonanoic acid had b.p. 239-241° (1.5 mm); m.p. 22-23° (from petroleum ether); n_D^{24} 1.4660.

Found %: C 68.11; 68.29; H 11.11; 11.10

$C_{26}H_{50}O_4S$. Calculated %: C 68.15; H 10.91

SUMMARY

1. The following compounds, not previously described, have been prepared by the action of sodium sulfide on polychloro derivatives of formula $CCl_2=CH(CH_2)_nCl$ and $CCl_3-CH_2-(CH_2)_nCl$: bis(3,3-dichloroallyl) sulfide, bis(5,5-dichloro-4-pentenyl) sulfide, bis(7,7-dichloro-6-heptenyl) sulfide, and bis(5,5,5-trichloropentyl) sulfide.

2. 7,7'-Thiodiheptanoic and 9,9'-thiodinonanoic acids, which have not been described previously, have been prepared by the action of sodium sulfide on the corresponding ω-chloro carboxylic acids. Their diethyl and dibutyl esters have been prepared.

Received May 30, 1953

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SOME REACTIONS OF 3,3,3- AND 1,1,3-TRICHLOROPROPENES

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Until recently 1,1,2-trichloropropene has been erroneously assigned the structure of 3,3,3-trichloropropene [1] and this has led to incorrect inferences concerning the reactivity of 3,3,3-trichloropropene. It has been stated that 3,3,3-trichloropropene appears to be unable to undergo the allyl rearrangement [2], to exchange the chlorines of its trichloromethyl group for fluorines [3], and to add hydrogen chloride and hydrogen bromide [4].

Two of the authors of the present paper together with Firstov [5] were the first to synthesize 3,3,3-trichloropropene from 1,1,1,3-tetrachloropropane, and they showed that it would undergo the allyl rearrangement, unite with chlorine and bromine, polymerize in presence of benzoyl peroxide, and condense with benzene in presence of aluminum chloride (in this reaction allyl rearrangement occurred). It was later shown that 3,3,3-trichloropropene combines, in presence of benzoyl peroxide, with bromotrichloromethane and with hydrogen bromide. In the course of this work we discovered a rearrangement involving the transfer of a chlorine atom in the intermediately formed radical [6].

1,1,3-Trichloropropene was first prepared in 1948 [7], but its reactions have received only a little study [5, 7]. In the present paper we describe the results of the reactions of certain nucleophilic and other reagents on 3,3,3-trichloropropene and 1,1,3-trichloropropene.

As nucleophilic reagents we have used diethylamine, sodiomalonic ester, sodium sulfide, and sodium methoxide. In the case of reaction with 1,1,3-trichloropropene replacement of the allyl chlorine by the nucleophilic residue of the reagent was observed. The reactions of 3,3,3-trichloropropene with nucelophilic reagents were always accompanied by allyl rearrangement, leading to the same compounds as those formed by the action of the same reagents on 1,1,3-trichloropropene. These reactions may be represented by the schemes:

$$\left.\begin{matrix} CCl_3-CH=CH_2 \\ CCl_2=CH-CH_2-Cl \end{matrix}\right\} \begin{cases} + (C_2H_5)_2NH \longrightarrow CCl_2=CH-CH_2N(C_2H_5)_2 \\ + NaCH(COOC_2H_5)_2 \longrightarrow CCl_2=CH-CH_2CH(COOC_2H_5)_2 \\ + Na_2S \longrightarrow (CCl_2=CH-CH_2)_2S \\ + CH_3ONa \longrightarrow CCl_2=CH-CH_2OCH_3 \end{cases}$$

The identity of the dichloro(diethylamino)propenes obtained from the two trichloropropenes by the action of diethylamine was shown by a mixture melting point test on their hydrochlorides.

The identity of the products obtained by the action of sodiomalonic ester on the two trichloropropenes, and their structure, were shown by conversion into glutaric acid by hydrolysis and decarboxylation. The identity of the bis(dichloropropenyl) sulfides obtained from the two trichloropropenes was established by a mixture melting point test on the sulfones prepared from these sulfides. By the action of sodium methoxide on 3,3,3-trichloropropene and on 1,1,3-trichloropropene, the same compound was obtained in each case, and it evidently had the structure 1,1-dichloro-3-methoxypropene; when it was treated with chlorine under very mild conditions, a pentachloro compound was formed which probably had the structure $CCl_3-CHClCHClOCH_3$.

It must be emphasized that the reactions of nucleophilic reagents with 3,3,3-trichloropropene proceed with good yield under conditions that preclude preliminary isomerization into 1,1,3-trichloropropene. It may be supposed that the center for nucleophilic attack in 3,3,3-trichloropropene is the methylene group, since the carbon of the trichloromethyl group is powerfully shielded by means of chlorine atoms. Hence, the reactions of 3,3,3-trichloropropene studied here belong to the type that occur with transfer of reaction center [8]. The reaction of 3,3,3-trichloropropene with diethylamine may be represented by the scheme:

$$(C_2H_5)_2\overset{\ominus}{N}H + \overset{\delta+}{C}H_2=CH-\overset{\delta+}{C}\begin{matrix} \nearrow Cl \\ \rightarrow Cl \\ \searrow Cl \end{matrix} \longrightarrow (C_2H_5)_2\overset{+}{N}H-CH_2-CH=CCl_2 + Cl^-$$

It is of interest to note that in the case of 3,3-dichloropropene reaction with nucleophilic reagents proceeds simultaneously in two directions: with and without isomerization [9]. This is evidently a consequence of the greater

accessibility of the carbon of the dichloromethyl group to nucleophilic attack. 3,3,3-Trichloro-2-methylpropene reacts with nucleophilic reagents with isomerization [10].

Also, a study has been made of the action of organomagnesium compounds on the isomeric trichloropropenes. In the reaction of butylmagnesium bromide both with 3,3,3-trichloropropene and with 1,1,3-trichloropropene, the main product was 1,1-dichloro-1-heptene, the structure of which was proved by hydrolysis to heptanoic acid. When the reaction was carried out with phenylmagnesium bromide, not only was 1,1-dichloro-3-phenylpropene obtained, but also biphenyl. It should be noted that these reactions, as is usual in reactions of a homolytic nature, proceed with formation of a number of other products, which were not investigated further.

When cuprous cyanide reacted with 3,3,3-trichloropropene and with 1,1,3-trichloropropene, the same product, 4,4-dichloro-3-butenenitrile, was obtained in each case in good yield. The identity of the two products was proved by preparation of the crystalline tetrachloride obtained by addition of chlorine, and also by a mixture melting point. The structure of the unsaturated nitrile was proved to be 4,4-dichloro-3-butenenitrile by hydrolysis of succinic acid. The crystalline tetrachloride had the structure 3,4,4,4-tetrachlorobutyronitrile, which was confirmed by the formation of 4,4,4-trichlorocrotononitrile by dehydrochlorination with alcoholic alkali.

By the action of Raney nickel on 3,3,3-trichloropropene in an ethanol medium, a tetrachlorohexadiene was obtained which apparently had the structure $(CCl_2=CH-CH_2-)_2$, since on hydrolysis in presence of concentrated sulfuric acid it yielded adipic acid, although in low yield.

Hence, also in reactions that are probably homolytic in nature, 1,1,3-trichloropropene reacts at the allyl chlorine and 3,3,3-trichloropropene reacts with allyl rearrangement.

The high reactivity of the trichloropropenes studied makes it possible to apply them to the synthesis of higher polychloroalkanes. Thus, 3,3,3-trichloropropene unites with polyhaloethylenes in presence of $AlCl_3$:

$$CCl_3-CH=CH_2 \xrightarrow{AlCl_3} \begin{cases} CH_2=CCl_2 \rightarrow CCl_2=CH-CH_2-CH_2-CCl_3 \\ CHCl=CCl_2 \rightarrow CCl_2=CH-CH_2-CHCl-CCl_3 \\ CHCl=CHCl \rightarrow CCl_2=CH-CH_2-CHCl-CHCl_2 \end{cases}$$

The structure of the product of the first reaction was established by hydrolysis to glutaric acid. The structures of the products of the other two reactions are suggested by analogy. It is interesting that, although 1,1,3-trichloropropene undergoes this reaction, the yields of the products are considerably less.

EXPERIMENTAL

Action of Diethylamine on 3,3,3-Trichloropropene

A solution of 10 g (0.055 mole) of 3,3,3-trichloropropene and 10 g (0.137 mole) of diethylamine in methanol was heated under reflux for eight hours. The alcohol was distilled off from a water bath, and the residue was dissolved in dilute hydrochloric acid and extracted with ether to remove neutral products. The hydrochloric acid solution was made alkaline in the cold with caustic soda solution, and the oil that separated was extracted with ether. The ether extract was dried with sodium sulfate. Vacuum distillation yielded 9.3 g (74%) of 3,3-dichloro-N,N-diethylallylamine, b.p. 65-66° (7 mm); n_D^{20} 1.4708; d_4^{20} 1.0693; found MR 47.56; calculated MR 47.73. A crystalline deposit formed in the substance after it had stood for a short time. The melting point of the hydrochloride of 3,3-dichloro-N,N-diethylallylamine was 139-140° (from alcohol + ether).

	Found %:	Cl 48.80; 48.80
$C_7H_{14}Cl_3N$.	Calculated %:	Cl 48.74

Action of Diethylamine on 1,1,3-Trichloropropene

A solution of 10 g (0.055 mole) of 1,1,3-trichloropropene and 11 g (0.150 mole) of diethylamine in methanol was heated for three hours. The reaction mixture was treated as above, and yielded 8.1 g (65%) of 3,3-dichloro-N,N-diethylallylamine, b.p. 65-66° (7 mm); n_D^{20} 1.4710; d_4^{20} 1.0694. Hydrochloride m.p. 139-140°. A mixture melting point test on the two hydrochlorides showed no depression.

Action of Sodiomalonic Ester on 1,1,3-Trichloropropene

1,1,3-Trichloropropene (30 g, i.e., 0.16 mole) was added under cooling (evolution of heat was observed) to sodiomalonic ester prepared from 3.2 g (0.20 mole) of malonic ester and 4.6 g of sodium in 70 ml of absolute ethanol. The reaction mixture was heated for three hours under reflux and cooled. Water was added until the

sodium chloride had dissolved, and the oil that separated was extracted with carbon tetrachloride, the extract being dried with magnesium sulfate. Vacuum distillation yielded 23.5 g (50%) of 3,3-dichloroallylmalonic ester, b.p. 102-103° at 1.5 mm, and 11.2 g of bis(3,3-dichloroallyl)malonic ester, b.p. 138-140° at 1.5 mm. 3,3-Dichloroallylmalonic ester had the following constants: n_D^{20} 1.4633; d_4^{20} 1.2135; found MR 61.09; calculated MR 60.95.

	Found %:	C 44.49; 44.66; H 5.28; 5.33
$C_{10}H_{14}Cl_2O_4$.	Calculated %:	C 44.62; H 5.24

The structure of 3,3-dichloroallylmalonic ester was proved by its hydrolysis with sulfuric acid to glutaric acid.

Bis(3,3-dichloroallyl)malonic ester melted at 39-40° (from petroleum ether).

	Found %:	C 41.56; 41.83; H 4.29; 4.30
$C_{13}H_{18}Cl_4O_4$.	Calculated %:	C 41.30; H 4.26

Action of Sodiomalonic Ester on 3,3,3-Trichloropropene

A mixture of sodiomalonic ester, prepared from 24 g of malonic ester and 3.5 g of sodium in 50 ml of absolute ethanol, and 21 g of 3,3,3-trichloropropene was heated under reflux for five hours. Fractionation of the reaction products yielded 16.3 g of 3,3-dichloroallylmalonic ester (n_D^{20} 1.4635; d_4^{20} 1.2135) and 10.6 g of bis(3,3-dichloroallyl)malonic ester, m.p. 39-40°, which gave no melting-point depression in a mixture test with the analogous product from the preceding experiment. When the dichloroallylmalonic ester was hydrolyzed with sulfuric acid, glutaric acid was again obtained.

Action of Sodium Sulfide on 3,3,3-Trichloropropene

A stirred mixture of 15 g of 3,3,3-trichloropropene with a solution of 12 g of $Na_2S \cdot 9H_2O$ in 70 ml of ethanol and 10 ml of water was heated for four hours. The alcohol was then removed (water bath), water was added to the residue, and the oil present was extracted with chloroform. Vacuum distillation yielded 10.1 g (62%) of bis(3,3-dichloroallyl) sulfide, b.p. 101-102° (2 mm); n_D^{20} 1.5628; d_4^{20} 1.4450.

Oxidation of the sulfide with excess of a solution of 30% hydrogen peroxide in glacial acetic acid yielded a sulfone, m.p. 113-114°; it gave no melting-point depression in a mixture test with bis(3,3-dichloroallyl) sulfone, prepared as described previously [11].

Action of Sodium Methoxide on 3,3,3-Trichloropropene

A mixture of 15 g (0.1 mole) of 3,3,3-trichloropropene and a solution of sodium methoxide prepared from 3 g of sodium and 50 ml of methanol was heated in a water bath for three hours. The reaction mixture was diluted with water, and the oil that separated was extracted with ether. The ether extract was washed with water and dried over calcium chloride. The material remaining after removal of ether was fractionated, and yielded 5 g of unchanged 3,3,3-trichloropropene and 7 g (50%) of a substance having b.p. 132-133°; n_D^{20} 1.4558; d_4^{20} 1.2117; found MR 31.62; calculated for $C_4H_5OCl_3$ MR 31.58.

	Found %:	C 34.27; 34.40; H 4.30; 4.41
$C_4H_5OCl_3$.	Calculated %:	C 34.07; H 4.29

Action of Sodium Methoxide on 1,1,3-Trichloropropene

To a sodium methoxide solution prepared by dissolving 3 g (0.18 mole) of sodium in 50 ml of methanol, 15 g (0.1 mole) of $CCl_2=CHCH_2Cl$ was added, a little at a time. Addition of the latter was accompanied by immediate precipitation of sodium chloride. The mixture was heated at the boil for one hour. The product was distilled from a Favorsky flask having a 50 cm fractionating column, and a fraction of b.p. 131-132° was collected (n_D^{20} 1.4558; d_4^{20} 1.2112). The methoxy compound so obtained was treated with chlorine at 60° in the dark. Not only addition, but also substitution occurred (evolution of HCl). Distillation of the chlorination product yielded 15 g of a substance having b.p. 97-98° (5.5 mm); n_D^{20} 1.5098; d_4^{20} 1.5749; found MR 46.77; calculated for $C_4H_5Cl_5O$ MR 46.65.

	Found %:	Cl 72.90; 72.94
$C_4H_5Cl_5O$.	Calculated %:	Cl 71.96.

The yield of the pentachlorocompound was 61% on the amount of trichloropropene taken.

Action of Cuprous Cyanide on 3,3,3-Trichloropropene

A stirred mixture of 50 g (0.34 mole) of 3,3,3-trichloropropene and 32 g (0.18 mole) of cuprous cyanide was heated in an oil bath under reflux, at first at 130°, and then at 160°. Heating was continued until liquid ceased to

drop back from the condenser. The product was distilled from the reaction mixture at 10 mm. A second distillation yielded 30 g (63.8%) of 4,4-dichloro-3-butenenitrile, b.p. 77-78° (11 mm); n_D^{20} 1.4831; d_4^{20} 1.3142; found MR 29.60; calculated for $C_4H_3Cl_2N$ MR 29.76.

	Found %:	C 35.52; 35.69; H 2.38; 2.49; Cl 51.75; 51.78
$C_4H_3Cl_2N$.	Calculated %:	C 35.32; H 2.22; Cl 52.14

Action of Cuprous Cyanide on 1,1,3-Trichloropropene

The reaction of 1,1,3-trichloropropene with cuprous cyanide proceeds in a similar manner: 15 g of 1,1,3-trichloropropene and 9 g of cuprous cyanide yielded 7.7 g of 4,4-dichloro-3-butenenitrile, b.p. 77-78° (11 mm); n_D^{20} 1.4831; d_4^{20} 1.3122. When they combine with chlorine, both the nitrile obtained from 3,3,3-trichloropropene and that from 1,1,3-trichloropropene yield the same tetrachlorobutyronitrile (see below), m.p. 44° (no depression in mixture test). In the reaction of 1,1,3-trichloropropene with potassium cyanide in an aqueous-alcoholic medium, only a very small yield of 4,4-dichloro-3-butenenitrile was obtained, a fact that may be associated with the instability of this nitrile in an alkaline medium.

Hydrolysis of $CCl_2=CH-CH_2CN$

A mixture of 2 g of the nitrile obtained in the preceding experiments and 10 ml of 90% sulfuric acid was heated at 100-120° until hydrogen chloride ceased to be evolved. The product was poured into water (100 ml). The aqueous solution was extracted with ether (fifteen 20 ml portions), and the ether extracts were dried over calcium chloride. The ether was removed, and the crystalline residue was recrystallized from water and washed with ether on the filter. The product was 0.7 g of succinic acid, m.p. 184-184.5°. In admixture with authentic succinic acid, it melted at 184-185°.

Addition of Chlorine to $CCl_2=CH-CH_2CN$

Through a solution of 33 g (0.24 mole) of $CCl_2=CH-CH_2CN$ in 70 ml of carbon tetrachloride, heated at the boil and illuminated with a 150-watt lamp, chlorine was passed to saturation. The solvent was distilled off, and the crystalline residue was vacuum-distilled. Practically the whole of the product came over at 105-107° at 6.5 mm. It melted, after recrystallization from petroleum ether, at 43.5-44°. The yield was 47.2 g (94%).

	Found %:	C 23.48; 23.43; H 1.58; 1.54
$C_4H_3Cl_4N$.	Calculated %:	C 23.22; H 1.46

Dehydrochlorination of $CCl_3CHCl-CH_2CN$

A solution of 5 g (0.089 mole) of KOH in 50 ml of methanol was added dropwise to an ice-cooled stirred mixture of 19 g (0.091 mole) of 3,4,4,4-tetrachlorobutyronitrile, prepared as described in the previous experiment, and 25 ml of the methanol. The mixture was set aside at room temperature overnight. The product was precipitated with water, separated, washed with water, dried with calcium chloride, and vacuum-distilled. The fraction boiling at 68-73° at 7 mm was collected. The yield of 4,4,4-trichlorocrotononitrile was 12.5 g (82%). In a second distillation almost the whole of the substance came over at 68-69° at 7 mm; n_D^{20} 1.5082; d_4^{20} 1.4237; found MR 35.70; calculated for $C_4H_2O_3N$ MR 34.62 (the literature [12] gives: n_D^{20} 1.5083, d_4^{20} 1.420).

	Found %:	Cl 62.42; 62.28
$C_4H_2Cl_3N$.	Calculated %:	Cl 62.41

When the reaction is carried out with an excess of alkali at a higher temperature, a molecule of alcohol adds to the trichlorocrotononitrile formed. For example, 44 g of the tetrachlorobutyronitrile treated with a solution of 15 g of KOH in 150 ml of methanol at room temperature yielded 28 g of a substance of b.p. 99.5° (6.5 mm); n_D^{20} 1.4820; d_4^{20} 1.3879; found MR 41.59; calculated for $C_5H_6Cl_3NO$ MR 41.35. The structure proposed for this compound is as follows:

$$CCl_3CHOCH_3-CH_2CN.$$

	Found %:	C 29.67; 29.78; H 3.12; 3.23
$C_5H_6Cl_3NO$.	Calculated %:	C 29.65; H 2.99

Action of Butylmagnesium Bromide on 3,3,3-Trichloropropene

An ethereal solution of butylmagnesium bromide, prepared from 17 g of butyl bromide and 3.7 g of magnesium in 50 ml of ether, was added slowly to a stirred cooled solution of 21 g of 3,3,3-trichloropropene. A precipitate of magnesium salts was formed. When addition of butylmagnesium bromide was complete, the reaction mixture

was heated for ten minutes, and was then cooled and poured into cold water. The ether solution was separated and dried with calcium chloride. Distillation yielded 12.8 g (68%) of 1,1-dichloro-1-heptene, b.p. 59-60° at 9 mm, and 4 g of a fraction boiling over the range 60-170° at 9 mm. The constants of 1,1 dichloro-1-heptene were n_D^{20} 1.4585; d_4^{20} 1.0427; found MR 43.76; calculated MR 43.79. Hydrolysis with sulfuric acid yielded heptanoic acid, from which the anilide, m.p. 64-65°, was prepared. In admixture with an authentic sample it melted at 64-65°.

Action of Butylmagnesium Bromide on 1,1,3-Trichloropropene

To an ethereal solution of butylmagnesium bromide, prepared from 17 g of butyl bromide and 3.7 g of magnesium in 50 ml of ether, 21 g of 1,1,3-trichloropropene was added. Heat was evolved, and the ether came to the boil. After 20-25 minutes, a precipitate of magnesium salts began to appear. The solution was heated in a water bath for two hours. Distillation of the reaction products yielded 6 g (31%) of 1,1-dichloro-1-heptene, b.p. 60-61° at 9 mm, and a large amount of a fraction boiling over the range 60-200° at 9 mm.

Action of Raney Nickel on 3,3,3-Trichloropropene

3,3,3-Trichloropropene (10 g) was gradually added to 6 g of Raney nickel in 20 ml of ethanol. Much heat was evolved, and it was necessary to provide cooling, so that the alcohol did not boil. The reaction mixture was then boiled for 20 minutes. The mixture was cooled, the nickel was removed, water was added to the alcoholic solution, and the oil that separated was extracted with chloroform. The chloroform solution was dried with calcium chloride. Vacuum distillation yielded 3.8 g (48%) of a tetrachlorohexadiene, b.p. 98-100° (8 mm); n_D^{20} 1.5149; d_4^{20} 1.3628; found MR 48.64; calculated MR 48.44.

	Found %:	C 32.90; 32.94; H 2.98; 2.92
$C_6H_6Cl_4$.	Calculated %:	C 32.72; H 2.72

When the tetrachlorohexadiene was hydrolyzed with sulfuric acid, adipic acid was obtained in low yield.

Addition of 3,3,3-Trichloropropene to 1,1-Dichloroethylene

3,3,3-Trichloropropene (15 g) was added gradually to a stirred mixture of 20 g of 1,1-dichloroethylene and 1 g of aluminum chloride at 15-20°. When addition was complete, the solution was stirred for a further 15 minutes and was then poured into water. The oil obtained was dried with calcium chloride. Vacuum distillation yielded 18.8 g (78%) of 1,1,5,5,5-pentachloro-1-pentene, b.p. 101-104° (12 mm); n_D^{20} 1.5125; d_4^{20} 1.4707; found MR 49.40; calculated MR 59.16.

	Found %:	C 24.42; 24.38; H 1.87; 1.94
$C_5H_5Cl_5$.	Calculated %:	C 24.73; H 2.06

By hydrolysis of the pentachloropentene with sulfuric acid, glutaric acid was obtained. In a similar way 3,3,3-trichloropropene and trichloroethylene yielded 1,1,4,5,5,5-hexachloro-1-pentene, b.p. 119-120° (10 mm); n_D^{20} 1.5291; d_4^{20} 1.5817; found MR 53.98; calculated MR 54.02.

	Found %:	C 21.45; 21.48; H 1.50; 1.68
$C_5H_4Cl_6$.	Calculated %:	C 21.66; H 1.44

From 1,2-dichloroethylene, 1,1,4,5,5-pentachloro-1-pentene was prepared; b.p. 105-107° (7 mm); n_D^{20} 1.5225; d_4^{20} 1.5077; found MR 48.89; calculated MR 49.16.

	Found %:	C 24.44; 24.40; H 1.85; 1.92
$C_5H_5Cl_5$.	Calculated %:	C 24.73; H 2.06

SUMMARY

1. A study has been made of the action of diethylamine, sodiomalonic ester, sodium sulfide, and sodium methoxide on 3,3,3-trichloropropene and 1,1,3-trichloropropene. It has been shown that in all cases, the reaction with 3,3,3-trichloropropene is accompanied by allyl rearrangement, so that the products are the same as those obtained by the action of the same reagents on 1,1,3-trichloropropene.

2. A study has been made of the action of organomagnesium compounds on 3,3,3- and 1,1,3-trichloropropenes. It has been shown that the alkylation of 3,3,3-trichloropropene is accompanied by allyl rearrangement.

3. A study has been made of the action of cuprous cyanide on 3,3,3- and 1,1,3-trichloropropenes, and it has been shown that in the case of 3,3,3-trichloropropene this reaction is accompanied by allyl rearrangement.

4. It has been found that in presence of $AlCl_3$ polyhaloethylenes unite with both 3,3,3-trichloropropene and 1,1,3-trichloropropene.

Received May 30, 1953

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DETERMINATION OF THE INDIVIDUAL HYDROCARBON COMPOSITION OF GASOLINES BY THE COMBINATION METHOD

COMMUNICATION 2. TWO GASOLINES FROM KAZANBULAK PETROLEUMS

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This paper * describes the results of a study of the individual hydrocarbon composition of two gasolines from Kazanbulak (Azerbaidzhan SSR) petroleums. The investigation was carried out by the previously described combination method [1]. This method, which was developed in the Zelinsky Institute of Organic Chemistry and the Lebedev Institute of Physics, is based on the principle of the gradual simplification of the composition of a mixture of hydrocarbons derived from these gasolines, so that it is finally possible to investigate them by the Raman-spectrum method. The obtaining of fractions containing hydrocarbons that are as homogeneous as possible with respect to the types of groups present and to molecular weight is achieved by the successive application at various stages of the investigation of exact rectification, chromatographic separation of aromatic hydrocarbons, and catalytic dehydrogenation of six-membered naphthenes with a view to their conversion into aromatic hydrocarbons and the subsequent separation of these.

We must make some reservations associated with the fact that the work described in this paper was carried out in 1948, when the combination method had not yet been worked out in all details. It was, in fact, on the basis of the experience gained during this investigation that the combination method began to take shape: the accuracy and completeness of analysis attained in this work has been considerably improved upon in later investigations, and in the investigation described in this paper the losses at all stages were appreciably higher than in subsequent investigations. We must also point out that the dehydrogenation catalyst used was of low activity. Also, at the time when this work was carried out we had not yet at our disposal many of the hydrocarbon standards that are so important for the complete quantitative, or even qualitative, analysis of gasolines with the aid of Raman spectra. Owing to these circumstances, the analysis of the gasolines discussed below is far from complete.

In spite of the incompleteness of the analysis, we consider that it is desirable to publish the results obtained, since in our opinion they are of definite interest even in such a form: actually, although the two Kazanbulak gasolines were obtained from petroleums having the same place of origin (at different horizons), they were found to differ greatly from one another in individual composition. Also, one of the gasolines differed considerably in composition from the other gasolines that we have investigated by this method. Hence, the analytical results for these gasolines, in spite of the deficiences pointed out above, enable us to extend our knowledge concerning the individual composition of Soviet gasolines.

The Kazanbulak petroleums that we studied were obtained directly from their source of origin. The scheme of investigation was completely identical with that given in the communication cited above [1], and the same letters are used to denote the fractions. The gasolines investigated will be denoted by TsK-1 and TsK-2.

As a result of our investigations more than 70 individual hydrocarbons were found in the two gasolines.

The numbers of hydrocarbons found and their distribution among the classes are given in Table 1. In Table 2 we give a list of the individual hydrocarbons found in Kazanbulak gasolines and their percent contents. It will be seen that 25 hydrocarbons have been determined quantitatively in the gasoline TsK-2, and this gasoline (which distilled over at temperatures ranging to 150°) was accounted for quantitatively to the extent of 55%. In the gasoline TsK-1, 33 hydrocarbons were determined quantitatively, but, owing to its more complex composition, only 40% of the whole gasoline (which distilled over at temperatures ranging to 150°) was accounted for quantitatively. Improvement in procedure and increase in the number of hydrocarbon standards has made it possible to account analytically for the compositions of gasolines to the extent of 80 - 90% in subsequent investigations.

* The first paper of this series if that by G. S. Landsberg and B. A Kazansky entitled "Determination of the Individual Composition of Straight-run Gasolines by the Combination Method" [1].

TABLE 1

Distribution of Hydrocarbons by Classes

Hydrocarbon class	No. of hydrocarbons detected in gasolines		No. of hydrocarbons determined quantitatively in gasolines		Total No. of hydrocarbons found in the 2 gasolines
	TsK-1	TsK-2	TsK-1	TsK-2	
Paraffins	29	28	16	10	41
Cyclopentanes	8	9	5	4	13
Cyclohexanes	11	9	6	6	11
Aromatics	6	5	6	5	6
Total	54	51	33	25	71

It will be clear from these results that TsK-1 contains an appreciably smaller amount of aromatic hydrocarbons than TsK-2. Also, TsK-1 is richer in branched paraffin hydrocarbons. But the difference between the two gasolines is particularly evident when an appraisal is made of the content of individual groups and classes of hydrocarbons, the total amount of all paraffin and naphthene hydrocarbons being taken as 100%. As will be seen from Table 3, although the overall percent content of paraffin hydrocarbons, differs little for the two gasolines, the nature of these paraffins differs greatly.

The gasoline TsK-1 contains a considerable amount of branched paraffins, including paraffins containing quaternary carbon atoms (more than 10%, i.e., more than in any of the gasolines that we investigated since), and contains practically no hydrocarbons of normal structure. On the other hand, the gasoline TsK-2 contains a considerable amount of normal paraffins and a small amount of branched hydrocarbons.

TABLE 2

Individual Hydrocarbons Found in the Gasolines TsK-1 and TsK-2

Hydrocarbon	Content (% by wt.)		Hydrocarbon	Content (% by wt.)	
	in TsK-1	in TsK-2		in TsK-1	in TsK-2
Paraffin hydrocarbons					
Butane	0.34	3.82	2,4-Dimethylhexane	1.72	+
Pentane	0.23	5.52	2,5-Dimethylhexane	0.55	+
2-Methylbutane	0.90	3.06	3,4-Dimethylhexane	+	–
Hexane	+	2.41	2,2,3-Trimethylpentane	++	–
2-Methylpentane	0.69	1.86	2,2,4-Trimethylpentane	+	–
3-Methylpentane	0.69		2,3,4-Trimethylpentane	0.57	–
2,2-Dimethylbutane	0.06	–	Nonane	–	+
2,3-Dimethylbutane	0.49	–	3-Methyloctane	–	+
Heptane	–	3.89	4-Methyloctane	–	+
2-Methylhexane	1.56	2.86	4-Ethylheptane	–	+
3-Methylhexane	1.56		3,3-Dimethylheptane	+	–
2,2-Dimethylpentane	1.07	–	3,4-Dimethylheptane	–	++
2,3-Dimethylpentane	4.37	–	3,5-Dimethylheptane	–	++
2,4-Dimethylpentane	1.32	–	4,4-Dimethylheptane	+	–
3,3-Dimethylpentane	++	–	2,3,5-Trimethylhexane	+	+
Octane	++	4.62	2,4,4-Trimethylhexane	–	+
2-Methylheptane	+	+++	3,3,4-Trimethylhexane	+++	++
3-Methylheptane	–	+++	2-Methyl-3-ethylhexane	+	++
3-Ethylhexane	+	+++	3-Methyl-3-ethylhexane	–	+
2,2-Dimethylhexane	2.85	–	3-Methyl-4-ethylhexane	–	+
2,3-Dimethylhexane	–	+	Total	19.0	28.0
Cyclopentane hydrocarbons					
Cyclopentane	0.10	0.60	Propylcyclopentane	+	–
Methylcyclopentane	0.08	1.92	Isopropylcyclopentane	++	–
Ethylcyclopentane	–	++	1-Ethyl-1-methylcyclopentane	–	+
cis-1,2-Dimethylcyclopentane	–	0.90	1-Ethyl-2-methylcyclopentane	–	++
			$1^c,2^c,3^c$-Trimethylcyclopentane	+	–
trans-1,2-Dimethylcyclopentane	–	1.43	$1^c,2^t,3^c$-Trimethylcyclopentane	2.62	+
1,3-Dimethylcyclopentane	2.77	–	$1^c,2^c,3^t$-Trimethylcyclopentane	0.70	+
			Total	6.3	4.9

TABLE 2 -- (continued)

Hydrocarbon	Content (% by wt.) in TsK-1	Content (% by wt.) in TsK-2	Hydrocarbon	Content (% by wt) in TsK-1	Content (% by wt) in TsK-2
Cyclohexane hydrocarbons					
Cyclohexane	0.53	2.03	Cyclohexane hydrocarbons C_8H_{16} including:	5.64	1.89
Methylcyclohexane	1.49	5.67			
Ethylcyclohexane	1.28	2.98			
1,1-Dimethylcyclohexane	++	+++	1-Ethyl-2-methylcyclohexane	+	+
1,2-Dimethylcyclohexane	2.34	2.01	1-Ethyl-3-methylcyclohexane	+	+
1,3-Dimethylcyclohexane	2.15	2.46	1-Ethyl-4-methylcyclohexane	+	–
1,4-Dimethylcyclohexane	0.29	0.30	1,2,4-Trimethylcyclohexane	+	–
			Total	13.7	17.3
Aromatic hydrocarbons					
Benzene	0.19	0.43	o-Xylene	0.08	0.19
Toluene	0.11	1.36	m-Xylene	0.06	1.54
Ethylbenzene	0.20	1.36	Cumene	0.14	–
			Total	0.8	4.9
Accounted for quantitatively				39.8	55.1
Not accounted for quantitatively, but partially accounted for qualitatively				37.1	20.7
Losses				16.8	21.7
Residues in flasks after fractionations				6.3	2.5
Total				100.0	100.0

NOTE. + indicates that the hydrocarbon was detected qualitatively in one fraction; ++ indicates that it was either detected in two fractions or was found in considerable amount in one fraction; +++ indicates that it was either detected in three fractions, or was detected in two, there being a considerable amount in one of these.

TABLE 3

Composition by Groups of the Paraffin–Naphthene Parts of the Gasolines TsK-1 and TsK-2 (% on the Gasoline)

Hydrocarbons	Gasolines TsK-1	Gasolines TsK-2
Normal paraffins	1.46	40.33
Paraffins having tertiary carbon atoms	37.01	15.49
Paraffins having quaternary carbon atoms	10.22	0
Cyclopentanes	16.09	9.66
Cyclohexanes	35.22	34.52

EXPERIMENTAL

Characteristics of Samples of Kazanbulak Petroleum. Petroleum No. 1 was a heavy viscous liquid having d_4^{20} 0.9127. Petroleum No. 2 was a liquid of relatively low viscosity, d_4^{20} 0.8330.

The Wide Cuts ShK-1 and ShK-2 and Their Fractionation. The gasoline samples referred to as wide cuts had the following properties: ShK-1, n_D^{20} 1.4345; d_4^{20} 0.7828; ShK-2, n_D^{20} 1.4200; d_4^{20} 0.7393.

The cuts were distilled through a 25-plate column, and the results of the fractionation are given in Tables 4 and 5 and in Fig. 1. It will be seen already by comparison of these curves that these gasolines differ considerably in chemical nature.

The main fractions of the two gasolines had the following properties: AK-1 – n_D^{20} 1.4150; d_4^{20} 0.7489; AK-2 – n_D^{20} 1.4110; d_4^{20} 0.7433.

The Fractions K_1, L, and A, i.e., all that came over below 150°, comprise the "whole gasoline", TsK-1 (2396.6 g) and TsK-2 (3967.5 g).

Investigation of the Gases and Light Fractions (K_1 and L). By fractionation of the gaseous part of K_1K-1 through a Podbielniak column it was established that the gas consisted of butane. From the course of the fractionation of LK-1 and the properties of the fractions obtained it was shown that LK-1 consisted of isopentane,

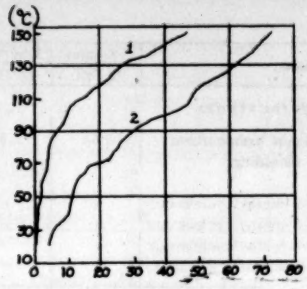

Fig. 1. Fractionation curves for the wide cuts: 1) ShK-1; 2) ShK-2.

pentane, 2,2-dimethylbutane, and cyclopentane (Table 2). In the gaseous part of K_1K-2 butane and some propane were found; in LK-2 isopentane and pentane were found (Table 2).

Separation of Aromatic Hydrocarbons from the Mixture of Paraffins and Naphthenes in the Main Fractions (A). In order to free the A fractions from aromatics, they were subjected to chromatographic analysis in columns filled with silica gel. As a result there were obtained aromatic fractions (B) and fractions consisting of paraffin and naphthenic hydrocarbons (C). The results of the separation are given in Table 6.

Investigation of the Aromatics (B). The aromatics that had been separated by chromatographic adsorption were fractionated through a column of about 40-plate efficiency. The results of the fractionation are given in Tables 7 and 8.

It will be seen from Tables 7 and 8 that Fraction I corresponds to benzene, Fraction II to toluene, Fraction III to xylenes and ethylbenzene, and Fraction IV to cumene. Fractions III and IV were investigated with the aid of Raman spectra. It was found that Fraction III of the aromatics BK-1 contained 60% (0.20% on TsK-1) of ethylbenzene, 22% (0.07% on TsK-1) of o-xylene, and 18% (0.06% on TsK-1) of m-xylene; Fraction IV contained 5% (0.01% on TsK-1) of o-xylene and 95% (0.14% on TsK-1) of isopropylbenzene. Fraction III of the aromatics BK-2 contained 44%

TABLE 4
Results of the Fractionation of the Gasoline ShK-1

Name of fraction	Boiling range (°C at 760mm)	Weight (g)	Content of fraction (% by weight)	
			in ShK-1	in TsK-1
Taken for fractionation	–	5644.0	100.0	–
K_1K-1 + LK-1 - light fraction with gaseous part	up to 53.0	46.9	0.8	1.96
AK-1 - main fraction	53.0-150.0	2349.7	41.6	98.04
O_{II}K-1 - residue	–	3156	55.9	–
Losses	–	91	1.7	–

TABLE 5
Results of the Fractionation of the Gasoline ShK-2

Name of fraction	Boiling range (°C at 760 mm)	Weight (g)	Content of fraction (% by weight)	
			in ShK-2	in TsK-2
Taken for fractionation	–	5552.0	100.0	–
K_1K-2 - gaseous part	–	166.7	3.0	4.20
LK-2 - light fraction	up to 50.2	396.8	7.1	10.00
AK-2 - main fraction	50.2-150.0	3404.0	61.3	85.80
O_{II}K-2 - residue	–	1520	27.4	–
Losses	–	64	1.2	–

TABLE 6
Chromatographic Separation of Fractions AK-1 and AK-2

Fraction	Amt. of fraction taken (g)	Results of separation								
		Aromatics (B)			Paraffin naphthene part (C)			Losses		
		(g)	(% in A)	(% in Ts)	(g)	(% in A)	(% in Ts)	(g)	(% in A)	(% in Ts)
AK-1	1305.3	10.65	0.82	0.80	1227.0	94.0	92.16	67.65	5.2	5.08
AK-2	1008.4	59.75	5.90	5.08	879.0	87.2	74.79	69.65	6.9	5.93

TABLE 7

Fractionation of the Aromatics BK-1

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction (% by wt.) in BK-1	Content of fraction (% by wt.) in TsK-1
Taken for fractionation		10,55			100,0	0,80*
I	78,1 - 100,9	2,55	1,4900	0,8533	24,2	0,19
II	100,9 - 129,7	1,5	1,4919	0,8580	14,2	0,11
III	129,7 - 145,2	4,4	1,4945	–	41,7	0,33
IV	145,2 - 154,0	2,0	1,4900	0,8604	19,0	0,15
Residue		0,05	–	–	0,5	0,01
Losses		0,05	–	–	0,4	0,01

TABLE 8

Fractionation of the Aromatics BK-2

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction (% by wt.) in BK-2	Content of fraction (% by wt.) in TsK-2
Taken for fractionation		19,1			100,0	5,08
I	78,8 - 102,1	1,6	1,4923	0,8619	8,4	0,43
II	102,1 - 128,9	5,1	1,4947	0,8624	26,7	1,36
III	128,9 - 141,8	9,6	1,4973	0,8650	50,3	2,55
Residue		2,0	1,4980	–	10,5	0,53
Losses		0,8	–	–	4,2	0,21

TABLE 9

Chromatographic Separation of the Catalyzates GK-1 and GK-2

Fraction	Amount of fraction taken (g)	Results of separation: Aromatics (g)	(% in D)	(% in Ts)	Paraffin-cyclopentane part (g)	(% in D)	(% in Ts)	Losses (g)	(% in D)	(% in Ts)
GK-1	339,8	51,2	15,1	12,81	275,7	81,1	68,84	12,9	3,8	3,23
GK-2	296,0	74,3	25,1	16,58	200,4	67,7	44,72	21,3	7,2	4,76

TABLE 10

Fractionation of the Aromatics DK-1

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction in DK-1 (% by wt.)	Content of corresponding cyclohexane hydrocarbons in TsK-1 (%)
Taken for fractionation		51,6			100,0	
I	77,8 - 103,2	1,7	1,4664	0,8150	3,3	0,45
II	103,2 - 129,7	4,8	1,4683	0,8241	9,3	1,27
III	129,7 - 146,9	22,1	1,4921	0,8578	42,8	5,80
IV	146,9 - 166,6	9,6	1,4988	0,8657	18,6	2,50
Residue		13,0	–	–	25,2	3,39
Losses		0,4	–	–	0,8	0,10

(1,36% on TsK-2) of ethylbenzene, 6% (0,19% on TsK-2) of o-xylene, and 50% (1,54% on TsK-2) of m-xylene; as the refractive indices of Fraction III and of the residue were nearly equal, it was assumed that they were of identical composition, and in this way the residue was taken into account in the analysis of the aromatics of the gasoline TsK-2. On the basis of all the results obtained, the contents of aromatic hydrocarbons in the whole gasolines were calculated and are given in Table 2.

* In this and succeeding tables the amount indicated is expressed as percent content of the whole of the given fraction in TsK 1 and TsK 2 and not of the portion taken for investigation.

TABLE 11

Fractionation of the Aromatics DK-2

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction in DK-2 (% by wt.)	Content of corresponding cyclohexane hydrocarbons in TsK-2 (%)
Taken for fractionation		74.8			100.0	
I	77.8-100.9	7.5	1.4916	0.8626	10.03	1.79
II	100.9-129.9	24.0	1.4917	0.8588	32.09	5.67
III	129.9-141.6	25.5	1.4949	0.8602	34.09	5.97
IV	141.6-146.2	5.9	1.5012	0.8731	7.89	1.39
V	146.2-166.7	5.6	1.4970	0.8680	7.49	1.30
Residue		4.2	–	–	5.61	0.98
Losses		2.1	–	–	2.80	0.50

TABLE 12

Fractionation of the Paraffin–Cyclopentane Part of EK-1

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	Content of fraction (% by wt.)		n_D^{20}	d_4^{20}	Aniline point (°C)
			in EK-1	in TsK-1			
Taken for fractionation		213.8	100.0	68.84			
I	48.8- 67.5	5.8	2.7	1.87	1.3761	0.6626	–
II	67.5- 88.0	8.5	4.0	2.74	1.3907	0.6953	64.5
III	88.0- 97.0	26.1	12.2	8.41	1.3982	0.7119	61.45
IV	97.0-107.2	17.2	8.0	5.54	1.4103	0.7439	58.65
V	107.2-110.0	10.7	5.0	3.44	1.4067	0.7331	64.7
VI	110.0-115.0	13.6	6.4	4.38	1.4063	0.7281	65.8
VII	115.0-120.0	20.5	9.6	6.60	1.4110	0.7372	62.1
VIII	120.0-125.0	15.0	7.0	4.83	1.4193	0.7583	56.4
IX	125.0-130.0	6.7	3.1	2.16	1.4200	0.7606	–
X	130.0-136.0	23.6	11.0	7.60	1.4160	0.7480	65.2
XI	136.0-138.0	25.6	12.0	8.24	1.4201	0.7575	65.2
XII	138.0-143.7	19.8	9.3	6.37	1.4225	0.7617	61.2
XIII	143.7-146.4	6.9	3.2	2.22	1.4287	0.7775	–
Residue		8.3	3.9	2.67			
Losses		5.5	2.6	1.77			

Dehydrogenation of Cyclohexane Hydrocarbons. The paraffin-naphthene parts of the gasolines (401.5 g of VK-1 and 366.7 g of VK-2) were dehydrogenated in order to convert the cyclohexane hydrocarbons into aromatics. Before dehydrogenation the C fractions had the following properties: VK-1: n_D^{20} 1.4145; d_4^{20} 0.7482; aniline point 61.3°; VK-2: n_D^{20} 1.4109; d_4^{20} 0.7349; aniline point 58.5°. Dehydrogenation was carried out over a specially prepared catalyst. The catalyzates obtained – 369.8 g of GK-1 (84.88% on TsK-1) and 323.9 g of GK-2 (66.06% on TsK-2)– had the following properties: GK-1: n_D^{20} 1.4254; d_4^{20} 0.7609; GK-2: n_D^{20} 1.4270; d_4^{20} 0.7548. The losses during dehydrogenation were 6.58% for TsK-1 and 7.71% for TsK-2.

Separation of the Catalyzates (D) into Aromatic Hydrocarbons and a Mixture of Paraffins and Cyclopentanes. The catalyzates D were separated by means of chromatographic adsorption into aromatic fractions (E) and fractions consisting of paraffin and cyclopentane hydrocarbons (F). The results of the separation are given in Table 9.

Investigation of the Aromatics (E). The aromatics separated were fractionally distilled through a column. The results of the fractionation and the properties of the fractions are shown in Tables 10 and 11.

It will be seen from Table 10 that Fraction I corresponds to benzene. Fractions III and IV were investigated optically, and it was found that Fraction III contained 36% of o-xylene, 37% of m-xylene, 5% of p-xylene, and 22% of ethylbenzene.

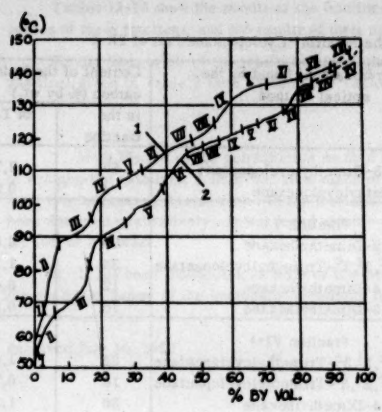

Fig. 2. Fractionation curves for the fractions EK-1 (1) and EK-2 (2).

About 10% of o-xylene was found in Fraction IV, and it was shown that 1-ethyl-2-methylbenzene and 1-ethyl-3-methylbenzene were also present in this fraction. The contents of the cyclohexane hydrocarbons corresponding to the aromatic hydrocarbons found are given in Table 2.

It follows from Table 11 that Fraction I corresponds to benzene, and Fraction II to toluene. Fractions III, IV, and V were investigated with the aid of Raman spectra. Fraction III was found to contain 40% of m-xylene, 10% of o- and p-xylenes, and 50% of ethylbenzene. Fraction IV contained 95% of o-xylene and 5% of m-xylene. In Fraction V 30% of o-xylene was found and it was shown that 1-ethyl-4-methyl-, 1-ethyl-2-methyl-, and 1-ethyl-3-methylbenzenes were present. The contents of the corresponding cyclohexane hydrocarbons are given in Table 2.

Investigation of the Paraffin-Cyclopentane Fractions (F). The F fractions separated by chromatographic adsorption had the following properties: EK-1 — n_D^{20} 1.4131; d_4^{20} 0.7422; EK-2 — d_4^{20} 0.7202. The F fractions were fractionated through a column having an efficiency of about 50 theoretical plates. As a preliminary, the fractionation curves were determined for these fractions by fractionation of separate 80-ml portions, and these curves are shown in Fig. 2. The F fractions (270-280 ml) were then fractionated into narrow fractions, which were investigated with the aid of their Raman spectra.

TABLE 13

Fractionation of the Paraffin–Cyclopentane Part of EK-2

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	Content of fraction (% by wt.)		n_D^{20}	d_4^{20}	Aniline point (°C)
			in EK-2	in TsK-2			
Taken for fractionation		198.6	100.0	45.80*			
I	36.1- 54.0	4.0	2.0	0.92	1.3888	0.6991	–
II	54.0- 66.0	9.9	5.0	2.29	1.3768	0.6659	66.8
III	66.0- 80.0	20.9	10.5	4.81	1.3913	0.6985	54.95
IV	80.0- 95.0	20.7	10.4	4.76	1.4000	0.7174	58.1
V	95.0-104.0	21.1	10.6	4.86	1.3967	0.7052	62.25
VI	104.0-115.0	14.3	7.2	3.30	1.4095	0.7377	68.0
VII	115.0-117.6	6.6	3.3	1.51	1.4041	0.7212	66.9
VIII	117.6-118.0	11.7	5.9	2.70	1.4042	0.7172	66.8
IX	118.0-122.0	9.9	5.0	2.29	1.4072	0.7261	64.35
X	122.0-124.5	9.7	4.9	2.24	1.4063	0.7249	64.75
XI	124.5-128.0	15.5	7.8	3.57	1.4033	0.7163	67.4
XII	128.0-133.5	6.6	3.3	1.51	1.4115	0.7352	65.0
XIII	133.5-137.0	11.7	5.9	2.70	1.4181	0.7518	67.0
XIV	137.0-140.0	7.1	3.6	1.65	1.4188	0.7514	64.6
XV	140.0-148.8	15.9	8.0	3.66	1.4141	0.7392	68.4
Residue		6.4	3.2	1.47			
Losses		6.6	3.4	1.56			

* Including the residue from the fractionation of the light fraction LK-2.

TABLE 14

Results of the Optical Investigation of Narrow Fractions of the Paraffin–Cyclopentane Part of EK-1

Hydrocarbons found by the optical method	Content of the hydrocarbon (% by wt.)		Hydrocarbons found by the optical method	Content of the hydrocarbon (% by wt.)	
	in the fraction	in TsK-1		in the fraction	in TsK-1
Fraction I			1,3-Dimethylcyclopentane	50	2.77
2,3-Dimethylbutane	26	0.49	Methylcyclohexane	4	0.22
2-Methylpentane	74*	0.69	Fraction V		
3-Methylpentane		0.69	2,2-Dimethylhexane	20	0.69
Fraction II			$1^c,2^t,3^c$-Trimethylcyclopentane	34	1.17
2,4-Dimethylpentane	48	1.32	2,4-Dimethylhexane	12	0.41
2,2-Dimethylpentane	39	1.07	2,5-Dimethylhexane	16	0.55
Cyclohexane	3	0.08	Fraction VI**		
Methylcyclopentane	3	0.08	$1^c,2^t,3^c$-Trimethylcyclopentane	33	1.45
Fraction III			$1^c,2^c,3^t$-Trimethylcyclopentane	16	0.70
2,3-Dimethylpentane	52	4.37	2,4-Dimethylhexane	30	1.31
2-Methylhexane	37*	1.56	2,3,4-Trimethylpentane	13	0.57
3-Methylhexane		1.56			
Fraction IV					
2,2-Dimethylhexane	39	2.16			

* About equal amounts.

** The remaining fractions were investigated qualitatively (see Table 2).

TABLE 15

Results of the Optical Investigation of Narrow Fractions of the Paraffin–Cyclopentane Part of EK-2

Hydrocarbons found by the optical method	Content of the hydrocarbon (% by wt.)		Hydrocarbons found by the optical method	Content of the hydrocarbon (% by wt.)	
	in the fraction	in TsK-2		in the fraction	in TsK-2
Fraction I			Fraction V		
Pentane	35*	0.32	Heptane	80	3.89
Cyclopentane	65	0.60	cis-1,2-Dimethylcyclopentane**	18	0.90
Fraction II			Fraction IX***		
2-Methylpentane	81**	1.86	Octane	30	0.69
3-Methylpentane			Fraction X		
Fraction III			Octane	60	1.34
Hexane	50	2.41	Fraction IX		
Methylcyclopentane	40	1.92	Octane	60	2.14
Fraction IV			Fraction XII		
2-Methylhexane	60	2.86	Octane	30	0.45
3-Methylhexane					
trans-1,2-Dimethylcyclopentane	30	1.43			
Cyclohexane	5	0.24			

* The quantitative optical analysis was made difficult by the small volume of the fraction. It was shown that cyclopentane was undoubtedly in excess. The quantitative estimation was made on the basis of the refractive indices and specific volumes of binary mixtures of pentane and cyclopentane.

** 3-Methylpentane predominated.

*** The Fractions VI-VIII and XIII-XV were investigated qualitatively (see Table 2).

Tables 12-15 show the results of the fractionation of the F fractions into narrow fractions, the physical properties of these fractions, and the results of their optical analysis.

On the basis of all of the results obtained, the contents of paraffin and cyclopentane paraffins in the whole gasolines given in Table 2 were calculated. Table 2 forms the general balance sheet for the whole investigation.

SUMMARY

1. With the aid of the combination method for the investigation of the individual hydrocarbon composition of straight-run gasolines, a study has been made of gasoline fractions derived from two petroleums originating from two horizons at Kazanbulak. In the fractions boiling below 150° more than 70 individual hydrocarbons have been detected qualitatively. It was found possible to account quantitatively for 55% of one of the gasolines and for 40% of the other.

2. It has been shown that, in spite of the closeness of the strata from which these petroleums were obtained, the chemical nature of the hydrocarbons forming their gasoline fractions differs very greatly.

Received July 10, 1953

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LITERATURE CITED

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DETERMINATION OF THE INDIVIDUAL HYDROCARBON COMPOSITION OF GASOLINES BY THE COMBINATION METHOD

COMMUNICATION 3. SURAKHAN GASOLINES

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In this paper we give the results of an investigation of two gasoline samples derived respectively from Surakhan first-grade and oil-grade petroleums. The previously described procedure was employed [1], as in the case of our investigation of two gasolines from Kazanbulak petroleums [2], the only difference being that the "whole" gasolines were not separated by laboratory distillation of the petroleums, but were taken from large-scale running.

As a result of detailed development work on the analytical procedure, in particular on the preparation of an active and reliable catalyst, and as a result also of increase in the number of available hydrocarbon standards for spectrum examination, it was possible in this investigation greatly to increase the extent to which the individual components of the gasolines could be accounted for quantitatively, and also to reduce losses considerably, as compared with the investigation described in the previous paper [2].

Both of the Surakhan gasolines contained a certain amount of sulfur compounds, and purification from these was not provided for in our procedure. This difficulty, however, was readily overcome, and the presence of sulfur compounds was without effect on the results of the investigation.

The gasoline derived from Surakhan first-grade petroleum, which will be denoted hereafter by TsS-1, was accounted for quantitatively to the extent of 77.8%, and the gasoline from Surakhan oil-grade petroleum, denoted hereafter by TsS-2, was accounted for quantitatively to the extent of 84.0%. The symbols used to denote the fractions are the same as those used in the papers cited above [1, 2].

TABLE 1

Distribution by Classes of Hydrocarbons Found

Hydrocarbon class	No. of hydrocarbons detected in gasoline		No. of hydrocarbons determined quantitatively in gasoline		Total No. of hydrocarbons found in the two
	TsS-1	TsS-2	TsS-1	TsS-2	
Paraffins	21	19	18	19	25
Cyclopentanes	8	8	7	8	10
Cyclohexanes	7	8	7	8	8
Aromatics	6	6	6	6	6
Total	42	41	38	41	49

In the two gasolines, 49 different hydrocarbons were detected. The distribution of these by classes is given in Table 1.

As will be seen from Table 1, the number of hydrocarbons accounted for quantitatively and qualitatively is practically the same for each gasoline. The number of hydrocarbons in each class is also the same for the two gasolines. The natures of these hydrocarbons, however, are considerably different for the two gasolines, and these differ considerably in their individual hydrocarbon compositions. This difference in composition will be readily seen from Table 2, in which the amounts of the individual hydrocarbons found in the gasolines under investigation are given.

TABLE 2

Individual Hydrocarbons found in the Gasolines TsS-1 and TsS-2

Name of hydrocarbon	Content (% by wt.)		Name of hydrocarbon	Content (% by wt.)	
	in TsS-1	in TsS-2		in TsS-1	in TsS-2
Paraffin hydrocarbons					
Methane	–	0.03	2,2-Dimethylpentane	0.28	0.22
Propane	0.08	–	2,4-Dimethylpentane	1.13	0.43
Butane	0.71	0.08	3,3-Dimethylpentane	0.68	–
Pentane	0.55	0.94	2,2,3-Trimethylbutane	0.28	0.11
2-Methylbutane	0.80	0.67	Octane	–	5.79
Hexane	0.62	3.82	2-Methylheptane	+?	5.70
2-Methylpentane	1.67	3.07	3-Methylheptane	+?	3.89
3-Methylpentane	0.60		4-Methylheptane	+	–
2,2-Dimethylbutane	0.44	0.19	2,2-Dimethylhexane	0.49	–
2,3-Dimethylbutane	1.07	0.38	2,3-Dimethylhexane	+	–
Heptane	+	6.40	2,4-Dimethylhexane	0.49	0.39
2-Methylhexane	3.16	3.01	2,5-Dimethylhexane	0.49	–
3-Methylhexane	1.91	2.01			
			Total	15.4	36.9
Cyclopentane hydrocarbons					
Cyclopentane	0.06	0.76	Ethylcyclopentane	+	0.39
Methylcyclopentane	4.59	2.88	$1^c,2^t,3^c$-Trimethylcyclopentane	2.05	–
1,1-Dimethylcyclopentane	0.96	–	1,2,4-Trimethylcyclopentane	3.45	4.28
cis-1,2-Dimethylcyclopentane	5.49	–	Propylcyclopentane	–	0.79
trans-1,2-Dimethylcyclopentane		3.01	Isopropylcyclopentane	–	0.53
1,3-Dimethylcyclopentane	1.91	2.00			
			Total	18.5	14.6
Cyclohexane hydrocarbons					
Cyclohexane	7.37	4.57	1,4-Dimethylcyclohexane	1.12	1.71
Methylcyclohexane	20.05	12.53	Ethylcyclohexane	2.23	2.28
1,1-Dimethylcyclohexane	2.99	1.20	1,1,3-Trimethylcyclohexane	–	0.52
1,2-Dimethylcyclohexane	1.12	2.19	Other cyclohexane hydrocarbons of composition C_9H_{18}	2.52	0.70
1,3-Dimethylcyclohexane	5.68	3.33			
			Total	43.1	29.0
Aromatic hydrocarbons					
Benzene	0.04	0.88	m-Xylene	0.18	0.59
Toluene	0.18	1.00	p-Xylene	0.12	0.25
o-Xylene	0.03	0.32	Ethylbenzene	0.28	0.45
			Total	0.8	3.5
Total hydrocarbons accounted for				77.8	84.0
Not accounted for quantitatively, but partially determined qualitatively				9.7	4.8
Losses				5.9	7.2
Residues in flasks from fractionations				6.6	4.0
Total				100.0	100.0

* + – hydrocarbon detected qualitatively.
+? – this hydrocarbon maybe present.

The gasoline from the first-grade petroleum contained about half as much paraffin hydrocarbons as that derived from the oil-grade petroleum. In the gasoline TsS-1, mainly branched paraffins were found (13.4% out of a total paraffin content of 15.4%), but in the gasoline TsS-2 approximately equal amounts of normal and branched paraffins were present (17.0% and 19.9%). There was a greater amount of paraffins having quaternary carbon atoms in the gasoline TsS-1 (2.05%) than in the gasoline TsS-2 (0.52%), but the greater part of the branched paraffins did not contain quaternary carbon atoms.

When the compositions of the gasolines are examined a group at a time, each group consisting of hydrocarbons of a particular molecular weight, it will be seen that in both gasolines all possible isomeric C_6 and C_8 hydrocarbons were present, apart from neopentane. In the C_7 group, heptane was found in the gasoline TsS-2, but was only detected qualitatively in the gasoline TsS-1; among the heptane isomers, 2,3-dimethylpentane and 3-ethylpentane were absent in both gasolines. Among the C_8 hydrocarbons, octane was found only in the gasoline TsS-2; hydrocarbons having one side chain were represented only by 2- and 3-methylheptanes, and there were only three having two side chains, namely 2,2-, 2,4-, and 2,5-dimethylhexanes; no highly ramified octane isomers were present. No C_9 hydrocarbons were found in either gasoline; it may therefore be supposed that the high-boiling part of the gasolines consisted mainly of naphthenic hydrocarbons.

An examination of the cyclopentane hydrocarbons indicates that the gasoline TsS-1 contained a considerably greater amount of disubstituted compounds (8.4%) than the gasoline TsS-2 (5.0%), in which the distribution of cyclopentane hydrocarbons according to weight was more even. The content of cyclohexane hydrocarbons, which was high in both of the gasolines, was about 50% higher in the gasoline derived from the first-grade petroleum than in that derived from the oil petroleum. The high content of methylcyclohexane (20.05% in TsS-1 and 12.53% in TsS-2) is particularly notable. The content of aromatic hydrocarbons was very low (0.8% and 3.5%), and was higher in the gasoline having the lower content of cyclohexanes (TsS-2).

EXPERIMENTAL

All of the fractions obtained in the course of the investigation were denoted by symbols, in accordance with the scheme given in a previous paper [1].

The original gasolines were fractionated through a column of 25-plate efficiency. The results of the fractionations and the properties of the original gasolines are given in Tables 3 and 4 and Fig. 1. In view of the fact that, as the fractionation showed, both samples were light gasolines, the final calculation of individual composition was based on the amounts of original gasolines. In this case, therefore, the original gasolines were "whole" gasolines (Ts).

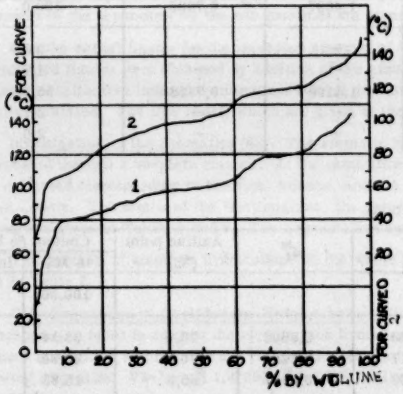

Fig. 1. Fractionation curves of the fractions ShS-1 (1) and ShS-2 (2).

In the fractionation of the original gasolines, three fractions were collected: the gaseous part K_1 (the condensate formed in traps cooled to −70°); the light fraction L (distillate obtained up to the temperature at which the first traces of benzene can be detected (positive formolite test)); and the fraction A (from the tail of Fraction L to 150°).

Investigation of the Gases in the Light Fractions (K_1 and L). In the case of the fraction K_1S-1, 6.6 g was taken for fractionation through a Podbielniak column, and it yielded 0.4 g of propane, 3.6 g of butane, and 2.6 g of high-boiling residue. It follows that the gasoline TsS-1 contained 0.08% of propane and 0.71% of butane. Owing to a mishap, the residue was not isolated from the main portion of the gas K_1.

No gas was found in the fraction LS-1, so that in this case the light fraction LS-1 corresponded to the debutanated light fraction MS-1.

The fractionation of the light part was carried out with a 50-plate column. Simultaneously with the collection of fractions, the fractionation curve was determined. Since all of the fractions obtained

contained small amounts (less than 0.1%) of sulfur compounds, the fractions were passed through silica gel in order to remove these. The sulfur compounds were thus separated from the hydrocarbons, and the former collected in the alcoholic part. The amounts of the fractions obtained and their properties after they had been freed from sulfur compounds are given in Table 5.

Since the mean boiling points, specific gravities, and refractive indices of Fractions I and II correspond respectively to the corresponding constants of 2-methylbutane (b.p. 27.85°; n_D^{20} 1.3537; d_4^{20} 0.6197), and pentane (b.p. 36.07°; n_D^{20} 1.3575; d_4^{20} 0.6262), the amounts of these fractions give the contents of these hydrocarbons in the gasoline.

Fraction III, as a study of its Raman spectra showed, contained 85% of 2,2-dimethylbutane and 15% of cyclopentane; from which it follows that the content of 2,2-dimethylbutane in the whole gasoline was 0.32%, and that of cyclopentane was 0.06%.

The residue from the fractionation of MS-1, which contained sulfur compounds, was passed for purification through silica gel, and was then united with the fraction VS-1 (see below).

TABLE 3

Fractionation of the Original Gasoline TsS-1

Fraction	Boiling range (°C at 760 mm)	Weight (g)	n_D^{20}	d_4^{20}	Content of fraction in TsS-1 (% by wt.)
Taken for fractionation		2132	1.4162	0.756	100.0
K_1S-1 (gaseous part)	–	28.4	–	–	1.3
LS-1 (light fraction)	27.3-57.6	51.0	–	–	2.4
AS-1 (main fraction)	57.6-150.0	1970.0	1.4148	0.7496	92.4
Residue	–	63.0	–	–	3.0
Losses	–	19.6	–	–	0.9

TABLE 4

Fractionation of the Original Gasoline TsS-2

Fraction	Boiling range (°C at 760 mm)	Weight (g)	n_D^{20}	d_4^{20}	Content of fraction in TsS-2 (% by wt.)
Taken for fractionation		1248	1.4097	0.7335	100.0
K_1S-2 (gaseous part)	–	6.6	–	–	0.5
LS-2 (light fraction)	29.5- 48.4	21.4	–	–	1.7
AS-2 (main fraction)	48.4-149.8	1186.8	1.4100	0.7358	95.1
Residue	–	8.6	–	–	0.7
Losses	–	24.6	–	–	2.0

TABLE 5

Fractionation of MS-1, and the Properties of the Fractions

Fraction No.	Boiling range (°C at 760 mm)	Weight (g)	n_D^{20}	d_4^{20}	Aniline point (°C)	Content (% by wt.) in MS-1	Content (% by wt.) in TsS-1
Taken for fractionation		51.0				100.00	
I	25.7-32.0	16.9	1.3533	0.6202	76.9	33.14	0.80
II	32.0-42.1	11.7	1.3577	0.6280	70.3	22.94	0.55
III	42.1-55.2	8.1	1.3763	0.6617	65.6	15.88	0.38
Residue		10.2	–	–	–	20.00	0.48
Losses		4.1	–	–	–	8.04	0.19

For the investigation of the fraction K_1S-2, 6.6 g was taken. Fractionation through a Podbielniak column yielded 0.39 g of methane, 0.12 g of intermediate fraction (C_3 and C_4 hydrocarbons), and 0.99 g of butane. It follows that for the whole gasoline, the methane content was 0.03% and the butane content was 0.08%.

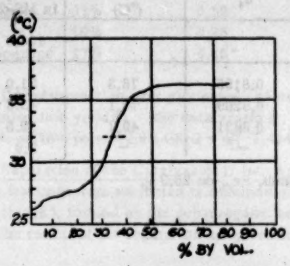

Fig. 2. Fractionation curve for the fraction MS-2.

As there was no gas component in LS-2, the residue from the fractionation of the gas K_1 was united to LS-2. Traces of sulfur compounds were present in MS-2, and the fraction was therefore passed through silica gel. The losses and the sulfur compounds amounted in all to 1.0 g. The light part, purified in this way, was fractionated through a 50-plate column. The results of the fractionation and the amounts of the fractions are shown in Table 6 and Fig. 2.

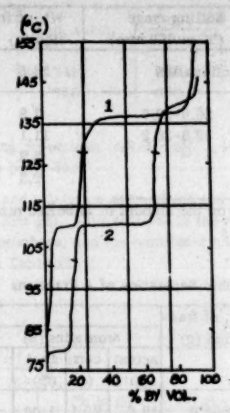

Fig. 3. Fractionation curves for the fractions BS-1 (1) and DS-1 (2).

The average boiling points specific gravities, and refractive indices of Fractions I and II corresponded to 2-methylbutane and pentane. The content of 2-methylbutane in the whole gasoline was 0.64%, and the pentane content was 0.91%. Owing to the small amount of residue, this was not investigated optically.

Separation of Aromatics from the Mixture of Paraffins and Naphthenes. The A fractions were subjected to chromatographic separation on silica gel, an aromatic part (B) and a paraffin-naphthene part (C) being isolated. The results of the separation for the two gasolines are given in Table 7.

Both the actual figures for the separated amounts of B and C and the corrected figures are given in Table 7; the corrected figures were obtained by addition of the amounts of the fractions used in tests for aromatic hydrocarbons and for refractive index determinations (which are not losses from the point of view of analysis) to the amounts actually separated. The true losses, which are given at the end of Table 7, amounted to a fraction of one percent.

Investigation of the Aromatics (B). The aromatic hydrocarbons separated with the aid of silica gel were fractionated through a 40-plate column. At the same time the fractionation curve was determined, and fractions were collected corresponding to benzene, toluene, and the xylenes. Fraction III was investigated with the aid of Raman spectra. The results of the fractionations, the properties of the fractions, and the results of the optical analysis are given in Tables 8 and 9. The fractionation curve for BS-1 is given in Fig. 3.

The contents of aromatic hydrocarbons in the whole gasolines, calculated on the basis of these results, are given in Table 2.

Dehydrogenation of Cyclohexane Hydrocarbons. The paraffin-naphthene parts (C) of the gasolines were dehydrogenated in order to convert the cyclohexane hydrocarbons into aromatics, so that they could be separated and their qualitative and quantitative composition determined. Before dehydrogenation the C fractions had the following properties: VS-1 $-n_D^{20}$ 1.4139; d_4^{20} 0.7485; aniline point 50.2°; VS-2 $-n_D^{20}$ 1.4067; d_4^{20} 0.7314; aniline point 56.7°.

The amounts of the C fractions taken for dehydrogenation and the amounts of the catalyzates obtained (D fractions) are given in Table 10. Again, as in Table 7, we give the actual and corrected amounts of D which were obtained by the introduction of corrections for the amounts of the D fractions used for refractive index determinations carried out during the dehydrogenation.

TABLE 6

Fractionation of MS-2, and Properties of Fractions

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Aniline point (°C)	Content (% by wt.) in MS-2*	Content (% by wt.) in TsS-2
Taken for fractionation		24.5				100.0	
I	26.0-32.0	7.9	1.3533	0.6195	76.3	31.0	0.64
II	32 0-36.2	11.1	1.3568	0.6269	70.1	43.6	0.91
Residue		3.2	1.3857	0.6831	49.7	12.5	0.26
Losses		2.3	–	–	–	9.0	0.19

* Calculated on the amount of M before removal of sulfur compounds, i.e., on 25.9 g.

TABLE 7

Chromatographic Separation of A Fractions

Fraction No.	Wt. of fraction (g)	Results of separation: aromatics (B) actual (g)	corr. (g)	in A (%)	in Ts (%)	paraffin-naphthene part (C) actual (g)	corr. (g)	in A (%)	in Ts (%)	losses (g)	in A (%)	in Ts (%)
AS-1	1865.0	18.6	20.1	1.00	0.92	1833.7	1834.3	98.35	90.87	10.6	0.65	0.61
AS-2	1118.9	43.5	43.8	3.80	3.61	1068.2	1068.4	95.39	90.72	6.7	0.81	0.77

TABLE 8

Fractionation of the Aromatics BS-1

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction (% in TsS-1)
Taken for fractionation		17.1	1.4946	0.8610	
I	78.7-100.0	0.7	1.4788	0.8431	0.04
II	100.0-127.2	3.5	1.4909	0.8548	0.18
III	127.2-145.7	11.35	1.4957	0.8639	0.61
Residue		0.3	–	–	0.02
Losses		1.25	–	–	0.07

Results of the Optical Analysis of Fraction III:

		Amt. in TsS-1 (% by wt.)
o-Xylene	5%	0.03
m-Xylene	30%	0.18
p-Xylene	20%	0.12
Ethylbenzene	45%	0.28

TABLE 9

Fractionation of the Aromatics BS-2

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction (% in TsS-2)
Taken for fractionation		41.4	1.4979	0.8675	
I	77.7 - 101.2	9.8	1.4998	0.8742	0.88
II	101.2 - 127.2	11.15	1.4971	0.8660	1.00
III	127.2 - 145.3	17.9	1.4980	0.8664	1.61
Residue		0.55	–	–	0.05
Losses		3.0	–	–	0.07

Results of the Optical Analysis of Fraction III are given on page 231.

Results of the Optical Analysis of Fraction III

		Amt. in TsS-2 (% by wt.)
o-Xylene	20%	0.32
m-Xylene	37%	0.59
p-Xylene	16%	0.25
Ethylbenzene	27%	0.45

TABLE 10

Amounts of the Fractions Taken and Obtained in the Dehydrogenation of BS-2 Aromatics

Fraction	Amt. taken	Amt. of D obtained (g)	
		Actual	Corr.
BS-1	742	699.0	699.5
BS-2	728	698.0	698.2

Dehydrogenation over platinized charcoal containing iron yielded the catalyzates D, which had the following properties: GS-1 – n_D^{20} 1.4410; d_4^{20} 0.7836; aniline point 12.9°; GS-2 – n_D^{20} 1.4240; d_4^{20} 0.7519; aniline point 35.5°.

Separation of the Catalyzates D into Aromatic Hydrocarbons and a Mixture of Paraffins and Cyclopentanes. The D fractions were subjected to chromatographic separation on silica gel. This resulted in the separation of the aromatics (E), formed by the dehydrogenation of cyclohexane hydrocarbons, and the paraffin-cyclopentane part (F). The results of the separation are given for the two gasolines in Table 11.

TABLE 11

Chromatographic Separation of the Catalyzates GS-1 and GS-2

Fraction	Amt. of catalyzates taken (g)	Results of separation					
		Aromatics (E)		Paraffin-cyclopentane part (F)		Losses	
		(g)	(% in D)	(g)	(% in D)	(g)	(% in D)
GS-1	677.0	300.0	44.31	373.0	55.10	4.0	0.59
GS-2	679.0	200.5	29.53	470.5	69.29	8.0	1.18

TABLE 12

Fractionation of the Aromatics DS-1

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}
Taken for fractionation		69.6	1.4964	0.8642
I	79.0 - 101.9	12.55	1.4992	0.8751
II	101.9 - 127.1	34.35	1.4962	0.8654
III	127.1 - 146.1	17.6	1.4971	0.8650
Residue		4.4		
Losses		0.8		

Results of the Optical Analysis of Fraction III

o-Xylene	11%
m-Xylene	56%
p-Xylene	11%
Ethylbenzene	22%

TABLE 13

Fractionation of the Aromatics DS-2

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}
Taken for fractionation		67.15	1.4960	0.8654
I	78.2 - 100.5	11.1	1.4972	0.8715
II	100.5 - 127.9	30.75	1.4948	0.8629
III	127.9 - 148.8	23.5	1.4967	0.8655
Residue		1.75		
Losses		0.05		

Results of the Optical Analysis of Fraction III

o-Xylene	23%
m-Xylene	35%
p-Xylene	18%
Ethylbenzene	24%

Owing to the high content of aromatics in the D catalyzates, their separation on silica gel was effected with the aid of a displacing liquid, isopentane. There was therefore no need to consume any of the investigated mixture of hydrocarbons in the refractive index determinations and formolite tests. The actually separated amounts of E and F, which are given in Table 11, were therefore used in the calculations.

Investigation of the Aromatics (E). The chromatographically separated aromatic hydrocarbons E were fractionated through a 40-plate column. Simultaneously fractionation curves were determined and fractions were collected corresponding to benzene, toluene, and the xylenes. The xylene fractions were investigated optically.

The results of the fractionations, the properties of the fractions, and the results of the optical analysis are given in Tables 12 and 13. The fractionation curve for DS-1 is given in Fig. 3.

Since the aromatic hydrocarbons E were obtained as a result of the dehydrogenation of the cyclohexane

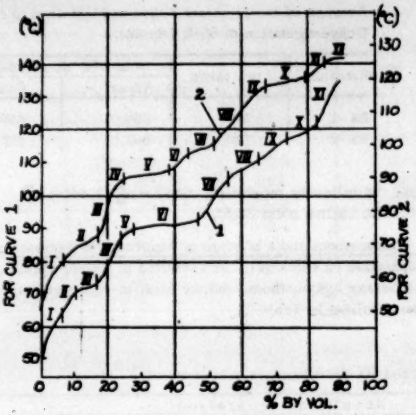

Fig. 4. Fractionation curves for the fractions ES-1 (1) and ES-2 (2).

hydrocarbons present in the gasoline, the benzene fractions of the aromatics E correspond to cyclohexane, the toluene fractions to methylcyclohexane, and the xylene fractions to dimethyl- and ethyl-cyclohexanes. From the results obtained relating to the amount and composition of the fractions of the aromatics E, taking into account the hydrogen removed in the dehydrogenation, the contents of the cyclohexane hydrocarbons in the gasolines were calculated.

The results of the calculation are given in Table 2, in which the results are summarized.

Investigation of the Paraffin-Cyclopentane Fractions (F). The paraffin-cyclopentane parts F, left after separation of the aromatics E by chromatographic adsorption, were fractionated through a 50-plate column. As a preliminary, the fractionation curve was determined for 100 ml of the F fraction of each gasoline (ES-1 and ES-2), the results being shown in Fig. 4. The vertical lines on the curves indicate the cuts.

The fractions obtained were characterized by their physical properties and analyzed with the aid of Raman spectra.

TABLE 14

Fractionation of the Paraffin-Cyclopentane Part of ES-1

Fraction No.	Boiling range (°C at 760 mm)	Weight of fraction (g)	Amt. of fraction in TsS-1 (% by wt.)	n_D^{20}	d_4^{20}	Aniline point (°C)
Taken for fractionation		217.1	47.20*	1.4047	0.7277	58.0
I	44.5 - 63.0	10.9	2.37	1.3735	0.6581	70.8
II	63.0 - 71.0	8.5	1.85	1.3822	0.6784	61.8
III	71.0 - 73.0	15.8	3.43	1.4052	0.7356	37.9
IV	73.0 - 86.5	13.0	2.83	1.3981	0.7048	56.2
V	86.5 - 90.0	8.8	1.91	1.4008	0.7206	58.1
VI	90.0 - 92.2	44.0	9.57	1.4032	0.7275	55.3
VII	92.2 - 105.0	17.2	3.74	1.4095	0.7409	51.1
VIII	105.0 - 111.0	22.7	4.93	1.4073	0.7346	62.3
IX	111.0 - 117.0	17.1	3.72	1.4073	0.7314	64.3
X	117.0 - 121.5	22.7	4.93	1.4117	0.7414	60.4
XI	121.5 - 133.0	9.8	2.13	1.4169	0.7542	59.0
XII	133.0 - 137.3	12.6	2.74	1.4172	0.7514	65.2
Residue		11.5	2.50	–	–	–
Losses		2.5	0.54	–	–	–

Tables 14, 15, 16, and 17 show the results of the fractionations, the physical properties, and the results of optical analysis. On the basis of these results the contents of paraffin and cyclopentane hydrocarbons in the whole gasolines were calculated.

The following took part in this investigation: senior laboratory assistant A. D. Matveeva and the laboratory assistants M. F. Zulina, T. V. Lapshina, V. A. Ovodova, K. G. Ryabova, and G. S. Taits.

SUMMARY

1. With the aid of the combination method for the investigation of the individual hydrocarbon composition

* Here and in Table 16 the amount indicated is the percent content in TsS-1 and in TsS-2 of the whole of the given fraction, and not for the portion taken for investigation.

TABLE 15

Results of the Optical Investigation of the Narrow Fractions of the Paraffin-Cyclopentane Part of ES-1

Hydrocarbons found by the optical method	Content (% by wt.) in the fraction	Content (% by wt.) in TsS-1
Fraction I		
2,3-Dimethylbutane	45	1.07
2-Methylpentane	45	1.07
2,2-Dimethylbutane	5	0.12
3-Methylpentane	Qualitatively	
Cyclopentane	Qualitatively	
Fraction II		
2-Methylpentane	65	0.60
3-Methylpentane	65	0.60
Hexane	15	0.28
Methylcyclopentane	20	0.37
Fraction III		
Methylcyclopentane	90	3.09
Hexane	10	0.34
Fraction IV		
Methylcyclopentane	40	1.13
2,4-Dimethylpentane	40	1.13
2,2-Dimethylpentane	Approx. equal	0.28
2,2,3-Trimethylbutane	Approx. equal	0.28
3,3-Dimethylpentane	Qualitatively	
Fraction V		
1,1 Dimethylcyclopentane	50	0.96
3,3-Dimethylpentane	35	0.68
2-Methylhexane	15	0.29
Fraction VI		
trans-1,2-Dimethylcyclopentane	30	2.87
cis- and trans-1,3-Dimethylcyclopentanes	20	1.91
2-Methylhexane	30	2.87
3-Methylhexane	20	1.91
Fraction VII		
cis- and trans-1,2-Dimethylcyclopentanes	70	2.62
Heptane	Qualitatively	
Ethylcyclopentane	Qualitatively	
Methylcyclohexane	Qualitatively	
Mixture of isomers of 1,3-dimethylcyclopentane	Qualitatively	
Fraction VIII		
1,2,4-Trimethylcyclopentane	70	3.45
2,2-Dimethylhexane	10	0.49
2,4-Dimethylhexane	10	0.49
2,5-Dimethylhexane	10	0.49
Fraction IX		
$1^c,2^t,3^c$-Trimethylcyclopentane	55	2.05
2,3-Dimethylhexane	Qualitatively	
Fraction X		
1,1-Dimethylcyclohexane	50	2.46
2-Methylheptane	Qualitatively	
3-Methylheptane	Qualitatively	
4-Methylheptane	Qualitatively	
Fraction XI		
1,1-Dimethylcyclohexane	25	0.53
Fraction XII		
Not investigated optically		

of gasolines, two gasoline samples, from first-grade and oil grade Surakhan petroleums respectively, have been analyzed.

2. The individual composition of the gasoline derived from first grade Surakhan petroleum has been accounted for quantitatively to the extent of 77.8%, and the gasoline from the oil-grade petroleum has been accounted for to the extent of 84.0%. Altogether, 47 hydrocarbons have been determined quantitatively in the two gasolines.

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[2] B. A. Kazansky, A. F. Plate, E. A. Mikhailova, A. L. Liberman, M. I. Batuev, T. F. Bulanova, and G. A. Tarasova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1954, No. 2, 266.*

* See Consultants Bureau Translation, page 215.

TABLE 16

Fractionation of the Paraffin-Cyclopentane Part of ES-2

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	Amt. of fraction in TsS-2 (% by wt.)	n_D^{20}	d_4^{20}	Aniline point (°C)
Taken for fractionation		213.5	60.3	1.3990	0.7132	62.8
I	43.0 - 65.0	13.5	3.81	1.3762	0.6758	66.8
II	65.0 - 72.2	20.8	5.88	1.3855	0.6858	57.7
III	72.2 - 83.5	7.7	2.17	1.4026	0.7289	44.6
IV	83.5 - 90.0	5.8	11.64	1.3962	0.7095	61.6
V	90.0 - 92.2	35.5	0.03	1.3979	0.7133	60.4
VI	92.2 - 97.0	5.4	1.53	1.3970	0.7094	61.2
VII	97.0 - 100.0	19.4	5.48	1.3906	0.6916	66.7
VIII	100.0 - 109.5	14.0	3.95	1.4063	0.7327	57.6
IX	109.5 - 117.5	18.3	5.17	1.4061	0.7292	64.9
X	117.5 - 120.0	25.8	7.29	1.4034	0.7197	67.4
XI	120.0 - 124.0	9.1	2.57	1.4097	0.7360	65.0
XII	124.0 - 127.0	14.7	4.15	1.4019	0.7156	68.1
XIII	127.0 - 136.3	9.3	2.63	1.4124	0.7408	65.8
Residue		11.0	3.10	1.4165	–	–
Losses		3.2	0.90	–	–	–

TABLE 17

Results of the Optical Investigation of the Narrow Fractions of the Paraffin-Cyclopentane Part of ES-2

Hydrocarbons found by the optical method	Content (% by wt.) in the fraction	Content (% by wt.) in TsS-2
Fraction I		
2-Methylpentane	65	2.48
3-Methylpentane		
Cyclopentane	20	0.76
2,3-Dimethylbutane	10	0.38
2,2-Dimethylbutane	5	0.19
Fraction II		
Methylcyclopentane	25	1.47
Hexane	65	3.82
3-Methylpentane	10	0.59
Fraction III		
Methylcyclopentane	65	1.41
2,2-Dimethylpentane	10	0.22
2,2,3-Trimethylbutane	5	0.11
2,4-Dimethylpentane	20	0.43
Fraction IV		
Not investigated optically		

TABLE 17 -- (continued)

Hydrocarbons found by the optical method	Content (% by wt.) in the fraction	Content (% by wt.) in TsS-2
Fraction V		
2-Methylhexane	30	3.01
3-Methylhexane	20	2.01
1,3-Dimethylcyclopentane	20	2.00
trans-1,2-Dimethylcyclopentane	30	3.01
Fraction VI		
Not investigated optically		
Fraction VII		
Heptane	95	5.21
Not accounted for	5	0.27
Fraction VIII		
Heptane	30	1.19
Ethylcyclopentane	10	0.39
1,2,4-Trimethylcyclopentane	30	1.18
2,4-Dimethylhexane	10	0.39
Not accounted for	20	0.80
Fraction IX		
1,2,4-Trimethylcyclopentane	60	3.10
2-Methylheptane	30	1.55
Not accounted for	10	0.52
Fraction X		
2-Methylheptane	50	3.64
3-Methylheptane	40	2.92
1,1-Dimethylcyclohexane	10	0.73
Fraction XI		
2-Methylheptane	20	0.51
Octane	40	1.03
3-Methylheptane	30	0.77
1,1-Dimethylcyclohexane	10	0.26
Fraction XII		
Octane	95	3.94
1,1-Dimethylcyclohexane	5	0.21
Fraction XIII		
Octane	30	0.79
Propylcyclopentane	30	0.79
Isopropylcyclopentane	20	0.53
1,1,3 Trimethylcyclohexane	20	0.52

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Received July 20, 1953.

SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS AND ACETYLENE

COMMUNICATION 7. PECULIARITIES OF THE REACTION OF ADDITION, CONTRARY TO MARKOVNIKOV'S RULE, OF HYDROGEN SULFIDE TO BUTYL VINYL ETHER

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When thiols react with vinyl ethers in sealed evacuated tubes, the addition reaction proceeds entirely in the direction contrary to Markovnikov's rule [1]. We have previously suggested [1] that in this case slight traces of oxygen act as catalyst, and that the reaction is a free-radical process, as in other cases of "anomalous" addition.

In the present investigation it has been shown that, when liquid hydrogen sulfide and butyl vinyl ether react under these conditions, the main products are 2-butoxyethanethiol (I) and bis(2-butoxyethyl) sulfide (II). By variation in the proportions of the ether and hydrogen sulfide, the reaction may be adjusted so as to give preferential formation of thiol or of sulfide, so that it is possible to synthesize either of these substances in fairly high yield:

$$CH_2{=}CHOC_4H_9 + H_2S \xrightarrow{-O-O-} \underset{(I)}{C_4H_9OCH_2CH_2SH} \qquad (1)$$

$$C_4H_9OCH_2CH_2SH + C_4H_9OCH{=}CH_2 \xrightarrow{-O-O-} \underset{(II)}{(C_4H_9OCH_2CH_2)_2S} \qquad (2)$$

The sulfide fraction, however, always contains some of the isomeric 1-butoxyethyl-2-butoxyethyl sulfide (IV), the amount of which increases with increase in the initial concentration of hydrogen sulfide. As we have already shown experimentally [1] that under the conditions of the experiment thiols add to vinyl ethers exclusively in violation of Markovnikov's rule, the source of the sulfide IV can only be addition of hydrogen sulfide to the vinyl ether in accordance with Markovnikov's rule, resulting in the formation of 1-butoxyethanethiol (III, Equation 3), which, owing to its high reactivity, will rapidly react "anomalously" with the ether (Equation 4):

$$CH_2{=}CHOC_4H_9 + H_2S \xrightarrow{H_2S} \underset{(III)}{CH_3CH(OC_4H_9)SH} \qquad (3)$$

$$CH_2{=}CHOC_4H_9 + CH_3CH(OC_4H_9)SH \xrightarrow{-O-O-} \underset{(IV)}{C_4H_9OCH_2CH_2SCH(OC_4H_9)CH_3} \qquad (4)$$

A knowledge of the amount of the sulfide IV formed, therefore, will enable us to calculate the proportion of the hydrogen sulfide molecules reacting in accordance with Markovnikov's rule. As will be seen from the results shown in Table 1 (Experimental Part), in the majority of the experiments it did not exceed 10%. Hence, in spite of statements in the literature [2], under mild conditions hydrogen sulfide may add to an ethylene bond mainly in the direction contrary to Markovnikov's rule (in presence of the catalysts that bring about the addition of thiols).

In the Experimental Part of this paper we show quite definitely that, as stated previously, the catalyst operative under these conditions consists of traces of oxygen dissolved in the vinyl ether. Direct proof of this is furnished by the considerable acceleration of the reaction induced by introduction into the tube of a quantity of dry oxygen, not exceeding 0.01% by weight (Table 3). The principal indirect proofs are: 1) the considerable reduction in the reaction rate, without effect on its direction, resulting from repeated distillation of the vinyl ether in a current of nitrogen before the experiment; 2) the complete inhibition of the reaction of anomalous addition in presence of the antioxidant hydroquinone, added in an amount of about 0.5% on the weight of the ether (Table 2). In presence of the antioxidant, addition to butyl vinyl ether in accordance with Markovnikov's rule is to be observed, and this

occurs not only with hydrogen sulfide (Equation 3), but also with the thiol formed (Equation 5), evidence for this reaction being provided by the appearance of bis(1-butoxyethyl) sulfide (V) in the reaction mixture.

$$CH_2{=}CHOC_4H_9 + CH_3{-}CH(OC_4H_9)(SH) \xrightarrow{H_2S} CH_3CH(OC_4H_9){-}S{-}CH(CH_3){-}OC_4H_9 \quad (V) \qquad (5)$$

Traces of oxygen, therefore, served as catalyst for "anomalous" addition. As will be shown below, the products of the oxidation of the vinyl ether have just the opposite effect on the reaction, and can therefore certainly not catalyze it.

The mechanism of "anomalous" addition may be represented by the usual scheme for a chain free-radical process [3]:

$$H_2S + {-}O{-}O{-} \longrightarrow HS^{\cdot} + HOO^{\cdot} \qquad (6)$$

$$CH_2{=}CHOR + HS^{\cdot} \longrightarrow HSCH_2\dot{C}HOR \qquad (7)$$

$$H_2S + HSCH_2\dot{C}HOR \longrightarrow HSCH_2CH_2OR + HS^{\cdot}\ \text{etc.} \qquad (8)$$

and further

$$HSCH_2CH_2OR + {-}O{-}O{-} \longrightarrow ROCH_2CH_2S^{\cdot} + HOO^{\cdot} \qquad (9)$$

$$CH_2{=}CHOR + ROCH_2CH_2S^{\cdot} \longrightarrow ROCH_2CH_2SCH_2\dot{C}HOR \qquad (10)$$

$$ROCH_2CH_2SH\ (\text{or } H_2S) + ROCH_2CH_2SCH_2\dot{C}HOR \longrightarrow (ROCH_2CH_2)_2S\ (\text{or } HS^{\cdot})\ \text{etc.} + ROCH_2CH_2S^{\cdot} \qquad (11)$$

The stages 6 - 8 (addition of hydrogen sulfide) are somewhat more rapid than the stages 9 and 10 (addition of thiol), since 2-butoxyethanethiol is almost always present in the reaction medium.

The free-radical addition reaction between hydrogen sulfide and butyl vinyl ether is distinguished by a number of peculiarities that cannot in any way be reconciled with Kharash's peroxide theory, and in this respect we again meet the situation found in the addition reaction between thiols and vinyl ethers that we studied previously [1]. Thus, we have established (Table 4), that oxidation products, formed by long storage of the ether in contact with the air, and also benzoyl peroxide and hydrogen peroxide, not only do not accelerate anomalous addition, but in fact, considerably retard it, which leads (depending on the initial concentration of hydrogen sulfide) either to complete inhibition of the process, or to addition of the residues of the sulfur compounds in accordance with Markovnikov's rule. It was found that suitable catalysts for anomalous addition were ascaridol (Table 6) and small amounts (about 0.1% by weight) of a concentrated solution of hydrogen chloride in dioxane, which contains a peroxide of unknown structure [4] (Table 5). This reaction, therefore, is characterized by specificity in its requirements with respect to the peroxide catalyst.

The behavior of this reaction toward molecular oxygen is very peculiar. Although slight traces of dissolved oxygen constitute a positive catalyst for the process of "anomalous" addition, its introduction into the reaction medium even in amounts of about 0.05% by weight has a marked inhibiting effect, and leads, as in the case of benzoyl peroxide and hydrogen peroxide, to the predominant formation of products in accordance with Markovnikov's rule (Table 3). Approximately the same amounts of oxygen, however, have been used by some authors [5] for the acceleration of the anomalous addition of HBr to allyl bromide, and no retarding effect was observed in this sytem of reactants. We may recall that Kharash and coworkers early suggested that peroxides and oxygen act exclusively as catalysts in anomalous addition reactions.

Our experiments show that the Kharash peroxide theory in its existing form is not valid in all liquid-phase addition reactions having a free-radical mechanism. Peroxides or oxygen are not always catalysts for free-radical addition reactions; their catalytic activity for certain systems is very specific, and evidently depends on the energy of formation, and therefore the method of formation, of the radical initiating the chain (in our case $RS^{\cdot}$, formed by Equations 6 and 9).

The chemical nature of the radical propagating the chain (in our case $RSCH_2\dot{C}HOR$) is of particular importance for the further course of the reaction, mainly with respect to its tendency to undergo oxidation or reduction reactions. From our point of view, the inhibiting effect of appreciable amounts of oxygen, and also of H_2O_2 and benzoyl peroxide, is to be associated with termination of chains due to ready oxidation, in accordance with Equations 12 and 13, of the radicals formed by Equations 7 and 10:

$$HSCH_2\dot{C}HOR + O_2 \longrightarrow HSCH_2CHOR \quad (12)$$
$$\quad\quad\quad

TABLE 1

Addition of Hydrogen Sulfide to Butyl Vinyl Ether in Absence of Specially Added Catalysts

Expt. No.	Amount taken		Experimental conditions			Unchanged ether (g)	Yield of reaction products				Amount of 1,2'-isomer in sulfide fr. (%)	α-Addition of H_2S (%)
	ether (g)	H_2S (moles per mole of ether)	total duration (days)	temperature (°C)	duration of heating (hr)		thiol (on ether)	sulfide (on ether)	total yield on ether	total yield on H_2S		
22	20	0.5	1	–	–	19.5	–	–	–	–	–	–
96	20.6	0.49	1.5	–	–	18.9	–	–	–	<10	–	–
90	20.5	0.47	5	–	–	9.0	37.0	55.0	92.0	76.5	5.5	~3
52	25	0.4	10	–	–	14.5	40.4	55.4	96.3	78	7.4	~4
91	20.3	0.48	13	–	–	7.2	27.7	62.7	90.4	80.0	2.5	~2
54	25	0.85	10	–	–	7.8	55.4	34.8	90.2	–	17.2	~6
47	25	0.4	5	60	30	6.4	6.8	87.7	94.5	97.0	1	~1
14	30	1.0	7	60	30	–	52.6	43.4	96.0	–	20.0	~9
46	25	1.2	4	60	30	1.1	56.1	36.8	92.9	–	18.5	~7

TABLE 2

Effect of Antioxidants and the Conditions of the Purification of the Starting Materials on the Reaction Between Liquid Hydrogen Sulfide and Butyl Vinyl Ether

Expt. No.	Amt. of H_2S (moles per mole of ether)	Experimental conditions				Unchanged ether (%)	Yield of reaction products (%)				Amt. of 1,2'-isomer in sulfide fr. (%)	α-Addition of H_2S (%)
		total duration (days)	temperature (°C)	duration of heating (hr)	method of purification of ether and H_2S; additives		thiol (on ether)	sulfide (on ether)	total yield on ether	yield on H_2S		
47	0.38	5	60	30	Standard	25.6	6.8	87.7	94.5	97.0	1	~1
38	0.31	3	75	17	Preliminary fractionation of H_2S through a Davis column [13]	37.3	11.3	78.3	89.4	86.7	1.5	~1
31	0.38	7	75	21	Ether distilled twice in a current of nitrogen	50.6	–	90.1	90.1	62.1	1.5	~1.5
57	0.37	7	60	36	Ether kept for 11 days over hydroquinone; distilled off on the day of the experiment (in the air)	31.6	7.8	84.5	91.3	90.9	5	~4
53	0.42	7	60	30	Hydroquinone (0.01 g) introduced into the tube	30.0	14.5	78.0	92.5	88.4	8.8	~6
49	0.39	4	60	30	Hydroquinone (0.1 g) introduced into the tube	92.0	50.0	–	50.0	9.0	–	–
46	1.2	4	60	30	Standard conditions	4.4	56.1	36.8	92.9	–	18.5	~7
56	1.2	7	60	36	Ether as in Expt. No. 57	11.2	60.7	34.2	94.9	–	20.2	~7
48	1.2	6	60	30	Hydroquinone (0.1 g) introduced into the tube	4.4	31.5	60.0	91.5	–	116*	(above 60%)

* Since the mixture of sulfides obtained in this experiment consisted of three isomers, the exact determination of the proportions by titration was impossible. This note applies also to all analogous cases given in the succeeding tables.

TABLE 3

Effect of Oxygen on the Addition of H_2S to Butyl Vinyl Ether (All experiments were carried out at room temperature with 20-25 g samples of ether)

Expt. No.	Amount taken		Duration of expt. (days)	Unchanged ether (%)	Yield of reaction products (%)				Amount of 1,2'-isomer in sulfide fr. (%)	Nature of thiol fraction	α-Addition of H_2S (%)
	H_2S (moles per mole of ether)	oxygen (ml/% by weight)			thiol (on ether)	sulfide (on ether)	total yield on ether	total yield on H_2S			
96	0.49	–	1.6	94	–	–	–	<10	–		
90	0.47	–	5	45	37.0	55.0	92.0	76.5	5.5	β	~ 1
91	0.48	–	13	35	27.7	62.7	90.4	80.0	2.5	β	~ 3
80	1.4	37/0.26	13	4	30.6	63.3	93.9	–	138	α + β	~ 1.5
81	0.38	28/0.15	13	27	12.5	80.7	93.2	99.0	129	α + β	~ 100
82	1.3	6.5/0.05	13	22	40.4	33.1	73.2	–	59.7	β + α	~ 20
83	0.44	6/0.04	13	50	33.6	47.0	80.6	65.8	48.8	β + α	~ 20
105	0.43	1.1/0.01	1.6	48	39.3	47.0	86.3	69.1	3.1	β	~ 1.5
98	0.45	0.7/0.005	6	34	33.7	55.3	89.0	90.1	5.8	β	~ 3

TABLE 4

Retarding Effect of the Oxidation Products of the Vinyl Ether and of Certain Peroxides on the Addition of H_2S Contrary to Markovnikov's Rule

Expt. No.	Amt. of H_2S (moles per mole of ether)	Experimental conditions				Unchanged ether (%)	Yield of reaction products (%)				Amt. of 1,2'-isomer in sulfide fr. (%)	α-Addition of H_2S (%)
		total duration (days)	temperature (°C)	duration of heat (hr)	method of purification of ether; added peroxides		thiol (on ether)	sulfide (on ether)	total yield on ether	total yield on H_2S		
47	0.38	5	60	30	Standard	25.6	16.8	87.7	94.5	97	1	~ 1
91	0.48	13	–	–	Standard	35.4	24.7	62.7	90.4	80.0	2.5	~ 2
66	0.36	4	60	30	Ether kept for a long time over potassium carbonate	44.4	35.9	52.8	88.7	94.4	3.2	~ 1.5
63	0.42	6	60	30	Ether kept for 36 days over sodium	53.2	42.6	43.1	85.7	72.5	7.4	~ 3
62	0.42	5	60	30	Ether kept for 80 days over sodium	48.0	45.8	30.2	76.0	79.0	12.0	~ 4
70	0.37	6	60	32	Benzoyl peroxide (0.02 g) introduced into the tube	68.5	27.1	70.4	97.5	52.5	62.2	> 50
60	0.36	12	–	–	Benzoyl peroxide (0.2 g) introduced into the tube	84	19.6	54.4	74.0	19.2	89.6	> 70
92	0.47	13	–	–	Hydrogen peroxide (27%, 0.2 ml) introduced into the tube	9.5	32.1	21.8	53.9	90.0	190	~ 100
17	0.63	8	70	30	Water (0.2 ml) introduced into the tube	3	24.6	73.9	98.5	–	8	~ 6

pressure of 15-16 atm so as to equalize pressures inside and out. After the reaction the tube was transferred with all necessary precautions from the autoclave to a Dewar flask containing liquid nitrogen, and was then opened in the chilled condition. The excess of hydrogen sulfide was evaporated off, and the reaction products were vacuum-fractionated.

When it was intended that the synthesis of sulfides should predominate, the reaction tube was placed in a closed metal tube and, in a number of experiments, was heated in a water thermostat for the necessary time. Breakage of the tube occurred only rarely, and was generally associated with bad sealing. Although practically the whole of the hydrogen sulfide was consumed by the end of the reaction in these experiments, the precaution was taken to open the tubes in the chilled condition. When the reaction products were fractionated, unchanged vinyl ether was trapped in a cooled coil, and the thiol and sulfide fractions were then collected. The sulfide fraction was titrated with 0.1 N NaOH after addition of mercuric chloride, as described previously [4]. When the experiments were carried out in presence of catalysts or other substances, these were dissolved beforehand in the ether, or were added directly to the tube.

In the accompanying tables the yields of reaction products are expressed in terms of the amount of ether that reacted, not the amount taken. The overall yield of products, therefore, does not give an indication of the extent to which the reaction proceeded, but shows the balance of products in the given experiment. The amount of unchanged ether is shown separately. In the experiments in which the amount of hydrogen sulfide taken was less than 0.5 mole per mole of the ether, the yield of products based on the amount of H_2S taken is also given, thus making it possible to obtain an idea of the extent to which it combines during the reaction.

1. Addition of Hydrogen Sulfide to Butyl Vinyl Ether in Absence of Specially Added Catalysts (in Presence of Traces of Oxygen). The optimum conditions for the synthesis of bis(2-butoxyethyl) sulfide were found to require the use of excess of the ether (1 mole to 0.4 mole of H_2S) and the application of heat. For the synthesis of 2-butoxyethanethiol, an excess of H_2S (more than 1 mole per mole of the ether) was required and the reaction was carried out in the cold. Table 1 gives the results of experiments with ether samples weighing 20-30 g; for bigger samples the time required for reaction was naturally longer. For example, for the synthesis of the sulfide from 100 g of the ether, heating must be for 80-90, not 30 hours.

Example. Experiment No. 47 (Table 1). Fractionation yielded 6.4 g of unchanged ether and:

Fraction I, b.p. 40- 43° (5 mm); n_D^{20} 1.4489; 1.7 g

Fraction II, b.p. 43-130° (5 mm); one or two drops

Fraction III, b.p. 130-132° (5 mm); n_D^{20} 1.4559; 19.1 g

Fraction I corresponded in boiling point and refractive index to 2-butoxyethanethiol, which we have synthesized previously [4]. With mercuric chloride it gave white crystals of the mercurichloride $C_4H_9OCH_2CH_2SHgCl$, m.p. 137.5-138° [4].

Analysis showed that Fraction III contained only about 1% of 1-butoxyethyl 2-butoxyethyl-sulfide, and its boiling point and refractive index corresponded to bis(2-butoxyethyl) sulfide $(C_4H_9OCH_2CH_2)_2S$, which we have synthesized previously [4]. Hence, under the conditions of the experiment, both hydrogen sulfide and 2-butoxyethanethiol added to butyl vinyl ether contrary to Markovnikov's rule.

2. Effect of Antioxidants and the Conditions of the Purification of the Starting Materials on the Reaction Between Liquid Hydrogen Sulfide and Butyl Vinyl Ether. Table 2 gives the results of comparative experiments having the object of determining the nature of the catalyst causing addition of hydrogen sulfide to butyl vinyl ether contrary to Markovnikov's rule. For comparison purposes, two standard experiments (No. 46 and 47) are given in which the reactants were purified in the usual way and no additions were made. In all of the experiments 25-30 g samples of the ether were used.

Prior distillation of the hydrogen sulfide (Expt. No. 38) did not have any essential effect on the character of the reaction and the reaction rate, and the addition catalyst, therefore, was not present as a contaminant in the hydrogen sulfide. In this experiment, distillation of the hydrogen sulfide was effected with the aid of a Davis column [13], the fraction of b.p. −60 to −59° being collected. The distilled hydrogen sulfide, which was collected in a cooled trap, was quickly evaporated and passed to the tube containing butyl vinyl ether, and the experiment was then carried out under standard conditions. Expt. No. 31 showed that distillation of the vinyl ether in a current of nitrogen, which reduced the amount of dissolved oxygen, considerably retarded the reaction (by a factor of two). Long treatment of the ether with hydroquinone followed by distillation on the day of the experiment (Expt. No. 57 and 56) had practically no effect on the character of the reaction (the distillation was performed not in a current of

TABLE 5

Addition of H_2S to Butyl Vinyl Ether Under the Catalytic Action of a Concentrated Solution of HCl in Dioxane (0.01 ml per 10 g of ether)

Expt. No.	Amount taken		Experimental conditions			Unchanged ether (g)	Yield of reaction products (%)				Amount of 1,2'-isomer in sulfide fr. (%)	α-Addition of H_2S (%)
	ether (g)	H_2S (moles per mole of ether)	total duration (days)	temperature (°C)	duration of heating (hr)		thiol (on ether)	sulfide (on ether)	total yield on ether	total yield on H_2S		
26	155	0.42	2	–	–	49.5	15.2	70.7	85.9	80.2	9	~ 6
6	70	0.43	3	–	–	10.7	11.0	79.0	90.0	98.0	4.2	~ 4
28	100	0.43	11	–	–	15.0	0.9	94.4	95.3	93.2	3.4	~ 3
7•	70	0.99	5	–	–	–	19.6	46.5	95.2	–	18.1	> 8
3•	40	1.35	1	70	8	–	54.3	36.8	91.1	–	31.8	> 11
16•	66	1.6	3	–	–	–	52.7	27.6	80.3	–	48	> 13
10•	60	2.0	2	–	–	–	68.2	19.1	87.3	–	40.7	> 8
15•	60	2.5	4	–	–	–	72.6	19.7	92.2	–	47	> 9
37••	24.3	0.45	6	60	26	1.5	–	78.3	78.3	–	47.6	~ 30
25•••	19.2	0.53	1	–	–	–	–	80.0	80.0	–	72.8	~ 50

• In Expt. No. 7, 3, 16, 10, 15 the thiol fraction contained some 1-butoxyethanethiol, so that the α-addition of H_2S was actually somewhat higher than that calculated from the titration of the sulfide part.

•• In this experiment 0.1 g of hydroquinone was introduced into the tube. Apart from a sulfide fraction containing all three isomers, decomposition products of these were obtained [4], namely 2.3 g of acetaldehyde dibutyl acetal and 1.5 g of acetaldehyde bis(2-butoxyethyl) mercaptal.

••• In this experiment the butyl vinyl ether used was first shaken for 27 hours in an atmosphere of dry oxygen. Here again 1.5 g of the acetal and 1.1 g of the mercaptal were obtained, and the sulfide fraction contained all three isomers.

TABLE 6

Addition of H_2S to Butyl Vinyl Ether Under the Catalytic Action of Ascaridol

Expt. No.	Amount taken			Experimental conditions			Unchanged ether (g)	Yield of reaction products (%)				Amount of 1,2'-isomer in sulfide fr. (%)	α-Addition of H_2S (%)
	ether (g)	H_2S (moles per mole of ether)	catalyst (g)	total duration (days)	temperature (°C)	duration of heating (hr)		thiol (on ether)	sulfide (on ether)	total yield on ether	total yield on H_2S		
77	60	1.55	0.65	6	–	–	4.2	63.4	33.1	94.5	–	7	~ 2
75	60	1.98	0.52	6	–	–	2.5	74.5	21.9	96.4	–	4	~ 1
74	60	2.03	0.60	6	–	–	2.2	69.0	24.1	93.1	–	1	~ 1
86	20	1.6	0.24	2	–	–	4	74.5	21.3	95.8	–	5	~ 1
101	20	2.13	0.3	2	–	–	1.2	77.0	13.8	90.8	–	1.5	~ 0.5
88	20	0.37	0.24	2	60	13.5	9.6	7.1	87.8	95.9	72.2	3.1	~ 2

nitrogen, but in the air); by this treatment the peroxide compounds in the ether itself were destroyed, but the amount of dissolved oxygen may have remained the same. Finally, in Expt. No. 53 the introduction of 0.01 g of hydroquinone (an amount insufficient to suppress the reaction) into the reaction medium somewhat increased the proportion of hydrogen sulfide molecules that added "normally", without effecting any essential change in the process as a whole. In Expt. No. 49 with a low concentration of hydrogen sulfide, the introduction of 0.1 g of hydroquinone practically stopped the reaction: during the standard time only 9% of the hydrogen sulfide reacted.

In Expt. No. 48 with a high concentration of hydrogen sulfide, the introduction of 0.1 g of hydroquinone resulted in the occurrence of addition mainly in the direction required by Markovnikov's rule. The thiol fraction consisted of a mixture of 1-butoxyethanethiol (1.1 g) and 2-butoxyethanethiol (7.4 g), and the sulfide fraction contained all three possible isomers. Titration showed that the content of bis(1-butoxyethyl) sulfide (V) (which yields two molecules of HCl in excess of a mercuric chloride solution [4]) in the sulfide fraction was not less than 16%, and that the total fraction of the hydrogen sulfide molecules that added in accordance with Markovnikov's rule was not less than 60%. The catalyst was in the nature of dissolved gas and appeared to be oxygen, since its action was paralyzed by the antioxidant hydroquinone.

3. Effect of Oxygen on the Addition of Hydrogen Sulfide to Butyl Vinyl Ether. Oxygen was passed from a graduated buret into the cooled tube, after it had been evacuated and immediately before it was sealed off. Expt. No. 105 and 98 (Table 3), when compared with the standard experiments, Expt. No. 96, 90, and 91, clearly demonstrate the catalytic acceleration of the reaction of anomalous addition of the sulfur-compound residues under the influence of small additions of oxygen, whereas Expt. No. 80-83 show the retarding effect of large additions of oxygen. In Expt. No. 80-83, the thiol fraction consisted of a mixture of 1- and 2-butoxyethanethiols, and the sulfide fraction consisted of a mixture of all three isomers, with a considerable predominance of α-addition products. In all experiments the yield of the thiol fraction was lower, and that of the sulfide fraction was higher, than in the standard experiments, behavior that is to be associated with the considerably higher reactivity of 1-butoxyethanethiol, as compared with its isomer. It will be quite clear than an excess of oxygen changes the direction of the reaction and increases its rate.

4. Retardation of the Anomalous Addition of Hydrogen Sulfide by Certain Peroxides. It will be seen from Expt. No. 62 and 63 (Table 4) that the ether, after prolonged standing over sodium (feeble peroxide reaction), gave rise to the following peculiarities: sulfide formation was considerably retarded, and the amount of the 1,2'-isomer in the sulfide fraction was increased. Ether that had been kept for a long time over potassium carbonate did not differ appreciably from the ether that had been given the standard purification (Expt. No. 66). Expt. No. 60, 70, and 92 showed that benzoyl peroxide and hydrogen peroxide produce a marked effect on the direction of the reaction: the yield of "normal" addition products was greatly increased, but, unlike oxygen, benzoyl peroxide caused a general retardation of the reaction. Expt. No. 17, which was carried out in presence of 0.2 ml of water, showed that water has no essential effect on the process, so that the effect produced by hydrogen peroxide could not have been due to the water present in this substance.

5. Addition of Hydrogen Sulfide to Butyl Vinyl Ether in Presence of a Solution of HCl in Dioxane. A comparison of the results given in Table 5 with those in Table 1 shows that the introduction of the HCl-dioxane catalyst considerably accelerates the "anlomalous" addition reaction, but increases the proportion of the hydrogen sulfide molecules that add in accordance with Markovnikov's rule to an insignificant extent. Expt. No. 37 shows that in this case some peroxide compound is acting as catalyst, for the introduction of hydroquinone, even at low hydrogen sulfide concentration, leads to a high yield of 1-butoxyethyl-2-butoxyethyl sulfide. In Expt. No. 25, the retardation of the "anomalous" reaction was brought about by peroxide compounds produced by agitation of the ether in an oxygen atmosphere for 27 hours. The HCl-dioxane catalyst accelerates the addition of H_2S to butyl vinyl ether, but it is particularly sensitive to oxygen and other contaminants, so that the results of the experiments are not always reproducible.

6. Addition of Hydrogen Sulfide to Butyl Vinyl Ether in Presence of Ascaridol. The most effective catalyst found for the anomalous addition of hydrogen sulfide to butyl vinyl ether was ascaridol. By the use of 0.1-0.13 g for each 10 g of the ether, we succeeded in accelerating this reaction considerably. The results of the experiments are given in Table 6.

SUMMARY

1. Methods have been developed for the synthesis of 2-butoxyethanethiol and bis(2-butoxyethyl) sulfide from butyl vinyl ether and hydrogen sulfide.

2. It has been shown that traces of oxygen (not more than 0.01% by weight), ascaridol, and the peroxide present in a concentrated solution of HCl in dioxane are catalysts for the addition of hydrogen sulfide to butyl vinyl ether contrary to Markovnikov's rule.

3. The free-radical nature of addition contrary to Markovnikov's rule is confirmed by the fact that it is retarded in presence of antioxidants.

4. It has been shown that a characteristic feature of the anomalous reaction is its inhibition by very small amounts of oxygen and peroxides, such as benzoyl peroxide, hydrogen peroxide, and the peroxide compounds formed during the storage of vinyl ethers.

5. It has been suggested that the inhibiting action of oxygen and peroxides is associated with the termination of chains resulting from the readily occurring secondary reaction in which radicals of the type $RSCH_2\dot{C}HOR$ (chain propagators) are oxidized.

Received February 10, 1953

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SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS AND ACETYLENE

COMMUNICATION 8. GENERAL METHOD FOR THE SYNTHESIS OF 2-ALKOXYETHANETHIOLS

M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro

We have shown in the preceding communication [1] that, by the action of liquid hydrogen sulfide on butyl vinyl ether in presence of traces of oxygen from the air, it is possible to effect the addition of sulfur compounds to this ether in the direction contrary to that required by Markovnikov's rule, i.e., with formation of 2-butoxyethanethiol and bis(2-butoxyethyl) sulfide:

$$CH_2=CHOC_4H_9 + H_2S \rightarrow C_4H_9OCH_2CH_2SH \quad (1)$$

$$CH_2=CHOC_4H_9 + C_4H_9OCH_2CH_2SH \rightarrow (C_4H_9OCH_2CH_2)_2S \quad (2)$$

We have extended this reaction to the following vinyl ethers: ethyl, propyl, isopropyl, isobutyl, isopentyl, octyl, and cyclohexyl vinyl ether. On the basis of the products obtained in the reaction we may draw some tentative conclusions concerning the reactivities of vinyl ethers having radicals of different structure in the RO group.

In general character, the reaction is the same for ethers in which R is an open-chain alkyl as for butyl vinyl ether. Thus, in most of the experiments the thiol fraction consisted almost entirely of 2-alkoxyethanethiol. The sulfide mixtures consisted of mixtures of the isomeric bis(2-alkoxyethyl) and 1-alkoxyethyl 2-alkoxyethyl sulfides in proportions that varied for different ethers, and only in exceptional cases did these mixtures contain any bis(1-alkoxyethyl) sulfide. Here, as in the case of butyl vinyl ether, it was found that as the initial hydrogen sulfide concentration was increased, there was an increase not only in the yield of thiol, but also in the yield of "normal" addition products. It may, therefore, be considered that the products of β-addition are formed by the overall reaction scheme expressed in Equations 3 and 4:

$$CH_2=CHOR + H_2S \xrightarrow{-O-O-} ROCH_2CH_2SH \quad (3)$$

$$CH_2=CHOR + ROCH_2CH_2SH \xrightarrow{-O-O-} (ROCH_2CH_2)_2S \quad (4)$$

and having a free-radical chain mechanism. 1,2'-Products are formed by a process expressed by Equations 5 and 6, in which the first equation expresses the ionic addition of hydrogen sulfide to the vinyl ether, and the second represents the free-radical addition of the 1-alkoxyethanethiol formed:

$$CH_2=CHOR + H_2S \xrightarrow[[H^+]]{H_2S} CH_3CH(SH)(OR) \quad (5)$$

$$CH_2=CHOR + CH_3CH(SH)(OR) \xrightarrow{-O-O-} CH_3CH(OR)(SCH_2CH_2OR) \quad (6)$$

Finally, 1,1'-dialkoxy sulfides are formed according to Equations 5 and 7 by reactions having an acid-catalyzed ionic character:

$$CH_2=CHOR + CH_3CH(SH)(OR) \xrightarrow[[H^+]]{H_2S} CH_3-CH(OR)-S-CH(OR)-CH_3 \quad (7)$$

Comparison of the proportions of reaction products under comparable conditions may thus provide a measure of the higher or lower tendency of any one of the ethers to react with hydrogen sulfide by the free-radical (Equation 3) or ionic (Equation 4) reaction.

The overall rate of addition of hydrogen sulfide to the alkyl vinyl ethers fell greatly as the chain length increased. The vinyl ethers having normal radicals (ethyl, propyl, and octyl vinyl ethers) nevertheless gave mainly the products of addition occurring in violation of Markovnikov's rule. The presence of branching in the radical led to still slower reaction and also to considerable increase in the yield of "normal" addition products; this behavior apparently depends on the greater tendency of these ethers to undergo ionic reactions (isopropyl, and particularly isobutyl and isopentyl, vinyl ethers). It is characteristic that for these ethers the retardation of the free-radical addition under the influence of the oxidation products accumulating during long storage of the ethers in contact with air, which had already been observed for the case of butyl vinyl ether [1], was still more marked. Also, even for the most carefully purified samples of isopentyl vinyl ether, it was not found possible to accelerate this process appreciably at room temperature by addition of ascaridol, which was fairly effective in the case of butyl vinyl ether [1]. Thus, vinyl ethers having branched radicals undergo addition in the direction contrary to Markovnikov's rule only with great difficulty.

The behavior of cyclohexyl vinyl ether in this reaction was peculiar (Table 10). In presence of traces of oxygen the addition reaction proceeded extremely slowly, but the yield of "normal" addition products in the sulfide mixture was very high (60-90%). Introduction of the HCl-dioxane catalyst [1] greatly increased the rate of addition, but, at the same time, led to reduction in the yield of the primary products, as a result of secondary processes (with formation of cyclohexanol, the acetal, and the mercaptal). With respect to its behavior in this reaction, therefore, the cyclohexyl ether is to be associated with the ethers having branched radicals.

The reaction between any alkyl vinyl ether and hydrogen sulfide in molecular proportions of 1:2 results in the synthesis of the corresponding 2-alkoxyethanethiol in 55-80% yield. We have thus developed a simple general method of synthesis of 2-alkoxyethanethiols from vinyl ethers.

EXPERIMENTAL

All of the vinyl ethers used in this work were purified by the usual method [2]. In the purification of the ethers, all the precautions shown to be necessary in the preceding communication [1] were taken, and they then gave practically negative tests for peroxide with ferrocyanide [3]. The ethers had the physical constants cited in previous papers from this laboratory [2, 4, 5].

The method of carrying out the addition of hydrogen sulfide is described in the preceding communication [1]. The reaction products consisted of 2-alkoxyethanethiols and mixtures of isomeric dialkoxy diethyl sulfides. In the first fractionation of the reaction product, the thiol fraction came over within a narrow range of temperature and was readily separated, owing to the great difference in boiling point, from the sulfide fraction. The mixture of sulfides was analyzed for the content of 1,2'- and 1,1'-isomers by a method based on their decomposition in presence of excess of mercuric chloride (as previously described in detail [6]).

From the titration results we calculated the percentage of "normally" uniting hydrogen sulfide molecules, and these are indicated in Tables 4-10 as percent "α-addition of H_2S". As in the preceding communication [1] we based the calculation on the fact that under the experimental conditions addition of thiols to vinyl ethers occurs, with rare exceptions, only in the direction contrary to Markovnikov's rule [7], so that "α-addition" products arise as a result of the "normal" reaction of hydrogen sulfide.

The pure bis(2-alkoxyethyl) sulfides were separated from the sulfide mixtures by a method in which the 1,2'-isomers were precipitated by means of an equimolecular amount of mercuric chloride [see the example of the purification of bis(2-propoxyethyl) sulfide]. The thiols were identified as mercurichlorides, and the sulfides as their complex salts with mercuric chloride. The physical properties and analyses of the substances synthesized are given in Tables 1-3. For the sake of completeness, these tables include also the 2-butoxy derivatives described in detail in previous communications [1, 6].

Of the mercury compounds given in Table 2, No. 1, 4, 5, and 6 were not analyzed, because their melting points were identical with those published by us previously, and no depression was given in mixture tests with the mercurichlorides previously synthesized by us by another method [6, 10]. The mercurichlorides No. 2, 3, 7, and 8 have not been described previously.

In Table 3 we give the properties of the bis(2-alkoxyethyl) sulfides synthesized; of these, the sulfides No. 1, 4, 5, and 6 have been previously prepared by us, and the constants given here coincide with those already published [6, 8, 10].* The constants given in the literature for sulfides No. 2 and 3 [11] are somewhat different from ours,

* We take this opportunity to correct regrettable misprints in previous communications [6], in which the boiling point of sulfide No. 1 was given incorrectly as 83.3-84.4° (3.5 mm), 83.8-84.4° (13.4 mm), instead of 83.8-84.4° (3.5 mm).

TABLE 1

No.	Formula	B.p. in °C (pressure in mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calculated	Analysis found C	Analysis found H	Analysis found S	Analysis calculated C	Analysis calculated H	Analysis calculated S
1	$C_2H_5OCH_2CH_2SH$	126-128 (760)	1.4456	0.9412	30.06	30.00	–	–	–	–	–	–
2	$n\text{-}C_3H_7OCH_2CH_2SH$	64 (40)	1.4478	0.9227	34.87	34.62	50.16 49.89	10.07 10.23	26.43 26.70	49.95	10.06	26.67
3	$iso\text{-}C_3H_7OCH_2CH_2SH$	56.1-56.4 (44)	1.4424	0.9136	34.84	34.62	50.19 50.17	10.22 10.10	26.40 26.44	49.95	10.06	26.67
4	$n\text{-}C_4H_9OCH_2CH_2SH$	48 (6)	1.4488	0.9111	39.50	39.24	–	–	–	–	–	–
5	$iso\text{-}C_4H_9OCH_2CH_2SH$	45.2-45.5 (9)	1.4444	0.9038	39.48	39.24	53.88 53.78	10.59 10.58	23.58 23.54	53.68	10.51	23.89
6	$iso\text{-}C_5H_{11}OCH_2CH_2SH$	53.9-54.5 (6)	1.4489	0.9028	44.01	43.86	57.07 57.30	11.11 11.06	21.56 21.74	56.70	10.88	21.66
7	$n\text{-}C_6H_{13}OCH_2CH_2SH$	103 (4.5)	1.4556	0.8906	58.05	57.71	63.41 63.10	11.79 11.87	16.85 16.85	63.10	11.65	16.83
8	$C_6H_{11}OCH_2CH_2SH$ (cyclohexyl)	73-73.5 (4.5)	1.4864	0.9938	46.33	46.28	60.06 59.98	10.12 10.11	20.15 20.12	59.95	10.06	20.01

Note: The literature gives: for the thiol 1) b.p. 125.5-128°, d_{20}^{20} 0.9479 [8]; for the thiol 2) b.p. 48-50° at 17 mm [9]; and for the thiol 4) b.p. 167° [9]. The remaining thiols have not been described.

owing, probably, to the presence of impurities in the author's products. The complex salts of the sulfides No. 1, 2, 3, and 5 were of the composition $(ROCH_2CH_2)_2S \cdot HgCl_2$; they were not analyzed, for their melting points coincided with the values previously published by us [6, 10] and with values given in the literature [8, 11]. The complex salt of the sulfide No. 8 had the composition $(C_6H_{11}OCH_2CH_2)_2S \cdot 2HgCl_2$.

Found %: C 22.97; 23.09; H 4.03; 3.77; Cl 17.17; 17.27 $C_{16}H_{32}O_2S \cdot 2HgCl_2$. Calculated %: C 23.16; H 3.65; Cl 17.09

The experiments on the addition of hydrogen sulfide to the individual ethers are summarized in Tables 4-10. The experiments for which no special indication is made were carried out without addition of catalyst, i.e., as we have shown previously, under the catalytic influence of traces of oxygen from the air. When a catalyst (HCl in dioxane [6] or ascaridol [1]) was used, it was always dissolved beforehand in the weighed sample of the ether. In all the tables the yields are calculated on the ether that reacted, not on the ether taken. For this reason, a separate indication is given in all tables of the amount of the vinyl ether recovered unchanged. Since the purification and separation of the reaction products were carried out similarly in all cases, detailed description has been confined to experiments on the addition of hydrogen sulfide to only two of the vinyl ethers (ethyl vinyl and propyl vinyl ethers).

I. Addition of Hydrogen Sulfide to Ethyl Vinyl Ether

The results of experiments on the addition of hydrogen sulfide to ethyl vinyl ether are given in Table 4. All of the experiments were carried out at room temperature. In Expt. No. 1, fractionation of the reaction products was carried out at atmospheric pressure and resulted in the partial decomposition of 1-ethoxyethyl 2-ethoxyethyl sulfide. In all of the remaining experiments the distillation was performed under reduced pressure.

Expt. No. 3. Ethyl vinyl ether (15.0 g) was placed in a tube having a constriction, and H_2S (9.7 g, i.e., 1.4 mole per mole of ether) was condensed in the tube as previously described [1]. The tube, while immersed in liquid nitrogen, was evacuated to a residual pressure of 4-5 mm (30 minutes), and sealed off while under vacuum. The tube was set aside for ten days at room temperature, and was then chilled in liquid

TABLE 2

No.	Formula	M.p. (in °C)	Analysis			
			found		calculated	
			C	H	C	H
1	$C_2H_5OCH_2CH_2SHgCl$	154.5-155.5	–	–	–	–
2	$n\text{-}C_3H_7OCH_2CH_2SHgCl$	137-137.5	17.06 17.04	3.23 3.27	16.90	3.12
3	$iso\text{-}C_3H_7OCH_2CH_2SHgCl$	153.5	16.83 16.63	3.28 3.33	16.90	3.12
4	$n\text{-}C_4H_9OCH_2CH_2SHgCl$	137,5-138	–	–	–	–
5	$iso\text{-}C_4H_9OCH_2CH_2SHgCl$	144-144.5	–	–	–	–
6	$iso\text{-}C_5H_{11}OCH_2CH_2SHgCl$	126	–	–	–	–
7	$n\text{-}C_5H_{11}OCH_2CH_2SHgCl$	126	28.28 28.28	4.81 5.01	28.24	4.98
8	$C_6H_{11}OCH_2CH_2SHgCl$ (cyclohexyl)	150.5	24.58 24.30	2.34 2.49	24.68	2.33

nitrogen and opened. Unchanged hydrogen sulfide was evaporated off. The increase in the weight of the reaction mixture resulting from bound (and, to some extent, dissolved) hydrogen sulfide was 5.4 g. Vacuum distillation yielded the following fractions:

Fraction I, b.p. 56-58° (60 mm); 13 g; n_D^{20} 1.4460

Fraction II, b.p. 58-100° (60 mm); 0.5 g

Fraction III, b.p. 91.5-92° (5 mm); 5.1 g; n_D^{20} 1.4556

After a second fractionation Fraction I came over completely at 126-128° (atmospheric pressure) and was found to be 2-ethoxyethanethiol, obtained in 58.9% yield (for constants see Table 1). The mercurichloride of this thiol melted at 154.5-155°*. After refractionation, Fraction III had b.p. 135-138° (50 mm); 83.8-84.4° (3.5 mm); 92.5-92.8° (6 mm); n_D^{20} 1.4555, i.e., constants very close to those of bis(2-ethoxyethyl) sulfide, previously synthesized by us [6], and also described in the literature [8, 11]. By titration with 0.1 N NaOH after addition of excess of mercuric chloride [6], the content of the isomeric 1-ethoxyethyl 2-ethoxyethyl sulfide in this fraction was found to be 7.7%. The yield of sulfide fraction was 27.5%.

Hence, under the experimental conditions used, ethyl vinyl ether reacts smoothly with hydrogen sulfide with formation mainly of addition products formed in violation of Markovnikov's rule.

II. Addition of Hydrogen Sulfide to Propyl Vinyl Ether

Results relating to the addition of hydrogen sulfide to propyl vinyl ether are given in Table 5.

Expt. No. 1. The experimental conditions are given in Table 5. Fractionation of the products yielded:

Fraction I, b.p. 60- 63° (37 mm); $n_D^{18.5}$ 1.4465; 42.0 g

Fraction II, b.p. 58-139° (24 mm); $n_D^{18.5}$ 1.4480; 1.1 g

Fraction III, b.p. 139-143° (24 mm); $n_D^{18.5}$ 1.4555; 19.6 g

After a second fractionation, Fraction I came over completely at 64-64.5° (40 mm), and was found to be 2-propoxyethanethiol $C_3H_7OCH_2CH_2SH$, obtained in 60.8% yield (for properties and analysis see Table 1). The mercurichloride $C_3H_7OCH_2CH_2SHgCl$ (fine white crystals) after recrystallization from boiling ethanol melted at 137-137.5° (see Table 2).

Fraction III consisted of a mixture of the sulfides $(C_3H_7OCH_2CH_2)_2S$ and $C_3H_7OCH_2CH_2SCH(OC_3H_7)CH_3$, for it gave a white precipitate with an ethanolic solution of mercuric chloride, and at the same time turned Methyl Orange red [6]. The content of 1,2'-isomer was found by titration to be 14.1%. After a second fractionation from a Favorsky flask, this mixture had: b.p. 103-106° (4 mm); n_D^{20} 1.4548; d_4^{20} 0.9326; found MR 60.01, calculated MR 59.73.

$C_{12}H_{26}O_2S$. Found %: C 58.07; 58.37; H 10.87; 10.91; S 15.36; 15.47
Calculated %: C 58.20; H 10.75; S 15.54

* No depression in admixture with our previously prepared sample [6].

TABLE 3

No.	Formula	B.p. in °C (pressure in mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calculated	Analysis found C	Analysis found H	Analysis found S	Analysis calculated C	Analysis calculated H	Analysis calculated S	M.p. of complex salt with $HgCl_2$ (°C)
1	$(C_3H_7OCH_2CH_2)_2S$	83.8-84.4 (3.5)	1.4560	0.9550	50.70	50.40	—	—	—	—	—	—	93-93.5
2	(n $C_3H_7OCH_2CH_2)_2S$	105.8 (4)	1.4553	0.9394	59.69	59.75	—	—	15.79 15.65	—	—	15.54	69-70
3	(iso-$C_3H_7OCH_2CH_2)_2S$	99-99.5 (6.0)	1.4493	0.9258	59.85	59.75	58.45 58.38	10.79 10.82	15.50 15.22	58.20	10.75	15.54	91-91.5
4	(n $C_4H_9OCH_2CH_2)_2S$	130-131 (4.9)	1.4560	0.9224	69.00	68.88	—	—	—	—	—	—	Liquid
5	(iso-$C_4H_9OCH_2CH_2)_2S$	125-126 (5)	1.4506	0.9130	69.13	68.88	—	—	—	—	—	—	47
6	(iso-$C_5H_{11}OCH_2CH_2)_2S$	144-145 (4)	1.4550	0.9089	78.49	78.1	—	—	—	—	—	—	Liquid
7	(n $C_5H_{11}OCH_2CH_2)_2S$	195-198 (3-3.5)	1.4610	0.9952	106.25	105.82	69.53 69.37	12.32 12.56	9.45 9.24	69.30	12.22	9.25	Liquid
8	$(C_6H_{13}OCH_2CH_2)_2S$ (cyclohexyl)	182-184 (5)	1.4982	1.0112	83.06	82.94	66.96 66.78	10.80 10.51	11.21 11.19	67.08	10.55	11.20	118

We made no attempt to fractionate this mixture, although we have already shown [6] that the separation of such sulfides by distillation is quite feasible, if a sufficiently efficient column is used.

The pure bis(2-propoxyethyl) sulfide was obtained by precipitating the whole of the 1,2'-isomer by means of mercuric chloride (see [6]). This was carried out by addition of 13 ml of a 20% solution of $HgCl_2$ in ethanol (slight excess over the amount of 1,2'-isomer present) to 12.2 g of this mixture of sulfides. The precipitate of the mercurichloride was filtered off after three days, and, after two crystallizations from boiling ethanol, it melted at 137-137.5° and gave no depression in admixture with the derivative obtained from the thiol. The filtrate was diluted with two parts of diethyl ether, and this solution was washed, first with water and then with caustic soda solution; the precipitate of HgO was filtered off, and the ether layer was again washed with water and then dried over calcined sodium sulfate.

Removal of ether yielded pure bis(2-propoxyethyl) sulfide having the constants given in Table 3; its complex salt with mercuric chloride melted at 69-70°. For bis(2-propoxyethyl) sulfide prepared by the action of zinc dust on bis(2-chloroethyl) sulfide in propyl alcohol, the literature [11] gives b.p. 243-247° (721 mm); n_D^{20} 1.4573; d_4^{20} 0.9439 and m.p. of the salt $(C_3H_7OCH_2CH_2)_2S \cdot HgCl_2$ −71°.

The main products of the reaction between H_2S and propyl vinyl ether were 2-propoxyethanethiol and bis(2-propoxyethyl) sulfide.

III. Addition of Hydrogen Sulfide to Isopropyl Vinyl Ether

The results given in Table 6 show that under the experimental conditions used isopropyl vinyl ether again gives mainly products of addition in the direction contrary to Markovnikov's rule. The amount of the 1,2'-isomer $_1C_3H_7OCH_2CH_2SCH(_1C_3H_7O)CH_3$ in the sulfide mixture was, however, somewhat higher than for the n-propyl vinyl ether.

IV. Addition of Hydrogen Sulfide to Isobutyl Vinyl Ether

The experimental results are given in Table 7.

In Experiments Nos. 1, 3, 4, and 5 the thiol fraction contained some 1-isobutoxyethanethiol $CH_3CH(OC_4H_9)SH$, for after the first fractionation it gave a yellowish precipitate with mercuric chloride [6, 12]. The same applies to the sulfide fractions, evidently contained mixtures of 2,2'-, 1,2'-, and 1,1'-isomers, so that it was not possible to determine their true compositions by titration [6]. Owing to the content of 1-alkoxy thiol in the thiol mixture, the actual percentage of the H_2S molecules adding in the "α" position was somewhat higher than that given in the last column, which is based on titration results. The yield of "normal" addition products was considerably higher for isobutyl vinyl ether than for other ethers, particularly in

TABLE 4

Expt. No.	Amount taken: of ether (g)	Amount taken: of H_2S (moles per mole of ether)	Duration of expt. (days)	Ether recovered (g)	Yield of reaction products (%): thiol	Yield of reaction products (%): sulfide	Yield of reaction products (%): total	Amount of 1,2'-sulfide in sulfide fr. (%)	α-Addition of H_2S (%)
1	20	1.4	60	1.1	57.4	23.9	81.3	~1	<1
2	25	0.4	10	14.0	38.3	35.4	73.7	1.3	~0.5
3	15	1.4	10	–	58.9	27.5	86.4	7.7	~2

experiments in which the H_2S concentration was high (Expt. No. 1 and 3), and the reaction rate was considerably lower (see Expt. No. 6). The ether used in Expt. No. 5 was preserved for six months over sodium and then distilled once before the experiment; it gave a distinct peroxide reaction. In this experiment addition was very much retarded, and the percent "α-addition" was very high.

V. Addition of Hydrogen Sulfide to Isopentyl Vinyl Ether

Isopentyl vinyl ether reacts very slowly with hydrogen sulfide (Expt. No. 1 and 5, Table 8). In all experiments the thiol fractions gave slightly yellowish precipitates with mercuric chloride, indicating the presence of 1-isopentyloxyethanethiol $CH_3CH(OC_5H_{11i})SH$ [6, 12], as in the case of isobutyl vinyl ether, so that the actual proportion of H_2S molecules adding in the α-position was somewhat higher than that calculated from results of the titration of the sulfide fraction. A particularly high content of "α-addition" products was given by the ether that had been kept for a long time over sodium (see Expt. No. 2). In this experiment the sulfide fraction contained not less than 32% of the 1,1'-isomer, which as shown previously [12], yields two molecules of HCl when treated with mercuric chloride. The thiol fraction, b.p. 38-48° at 4 mm, gave an egg-yellow precipitate with mercuric chloride, i.e., consisted mainly of the thiol $CH_3-CH(OC_5H_{11i})SH$. Ascaridol (Expt. No. 7) did not appreciably accelerate the reaction between hydrogen sulfide and isopentyl vinyl ether at room temperature.

TABLE 5

Expt. No.	Amount taken: of ether (g)	Amount taken: of H_2S (moles per mole of ether)	Experimental conditions: total duration (days)	Experimental conditions: temp. at which heated (°C)	Experimental conditions: duration of heating (hr.)	Ether recovered (g)	Yield of reaction products (%): thiol	Yield of reaction products (%): sulfide	Yield of reaction products (%): total	Amt. of 1,2'-sulfide in sulfide fr. (%)	α-Addition of H_2S (%)
1	49.5	1.2	65	–	–	–	60.8	33.1	93.9	14.1	5
2	15.0	2.9	97	–	–	–	80.0	16.1	96.1	19.2	3
3	15.0	2.6	5	70	18	0.2	70.5	18.1	88.6	47.4	14
4	15.0	0.5	5	70	18	3.1	29.2	56.1	85.3	11.7	6

VI. Addition of Hydrogen Sulfide to Octyl Vinyl Ether

The experiments in Table 9 show that, in presence of traces of oxygen, octyl vinyl ether unites slowly with hydrogen sulfide, but almost entirely in the direction contrary to Markovnikov's rule. When attempts were made to accelerate the reaction by introduction of an HCl-dioxane catalyst (Expt. No. 2 and 3), an appreciable yield of "normal" addition products was obtained.

VII. Addition of Hydrogen Sulfide to Cyclohexyl Vinyl Ether

As will be seen from Table 10, cyclohexyl vinyl ether unites with hydrogen sulfide still more slowly than isopentyl vinyl ether does, and it gives a still higher yield of addition products formed in accordance with Markovnikov's rule.

In Expt. Nos. 4-6 catalyst (27% HCl in dioxane) was added. In Expt. Nos. 3, 4, and 5, apart from the thiol and sulfide indicated in the tables, decomposition products were obtained: cyclohexanol, b.p. 160-162°, and a high-boiling residue, which decomposed when distilled and corresponded closely in analysis to the mercaptal $CH_3CH(SCH_2CH_2OC_6H_{11})_2$.

TABLE 6

Expt. No.	Amount taken		Experimental conditions			Ether recovered (g)	Yields of reaction products (%)			Amount of 1,2'-sulfide in sulfide fr. (%)	α-Addition of H_2S (%)
	of ether (g)	of H_2S (moles per mole of ether)	total duration (days)	temp. at which heated (°C)	duration of heating (hr.)		thiol	sulfide	total		
1	28.2	1.1	68	–	–	–	58.5	35.0	93.5	28.5	~10
2	10.0	0.5	12	70	26	3.8	–	89.2	89.2	10.6	~ 9
3	20.5	2.0	12	70	26	–	70.2	19.1	89.3	22.6	~ 4

TABLE 7

Expt. No.	Amount taken		Experimental conditions			Ether recovered (g)	Yields of reaction products (%)			Amount of 1,2'-sulfide in sulfide fr. (%)	α-Addition of H_2S (%)
	of ether (g)	of H_2S (moles per mole of ether)	total duration (days)	temp. at which heated (°C)	duration of heating (hr.)		thiol	sulfide	total		
1	15	2.3	8	70	27	–	54.2	25.0	79.2	70.1	>17
2	15	0.5	9	70	27	3.5	31.3	66.2	97.5	19.5	~13
3	20	1.0	12	70	58	–	34.3	51.7	86.0	45.5	>23
4	15	1.4	63	Room	–	–	36.7	51.1	87.8	29.5	>15
5	62	0.9	60	"	–	40.9	48.3	14.9	63.2	62.7	> 9
6	15	1.3	14	"	–	12.0	27.5	28.5	65.0	Not determined	

TABLE 8

Expt. No.	Amount taken: of ether (g)	Amount taken: of H_2S (moles per mole of ether)	Experimental conditions: total duration (days)	Experimental conditions: temp. at which heated (°C)	Experimental conditions: duration of heating (hr.)	Ether recovered (g)	Yields of reaction products (%): thiol	Yields of reaction products (%): sulfide	Yields of reaction products (%): total	Amount of 1,2'-sulfide in sulfide fr. (%)	α-Addition of H_2S (%)
1	20.0	0.7	75	–	–	18.9	77.0	–	77.0	–	–
2	40.0	2.4	64	–	–	–	44.4	43.8	88.2	131.8	~100
3	14.7	1.3	6	70	27	8.1	58.4	21.1	79.5	64.2	> 13
4	20.0	1.3	30	70	116	3.8	61.3	28.6	89.9	37.2	> 11
5	18.4	0.6	45	70	170	13.5	–	78.0	78.0	10.6	~ 8
7	20.0	0.7	7	–	–	18.5	–	–	–	–	–

TABLE 9

Expt. No.	Amount taken: of ether (g)	Amount taken: of H_2S (moles per mole of ether)	Amount taken: of catalyst (ml)	Experimental conditions: total duration (days)	Experimental conditions: temp. at which heated (°C)	Experimental conditions: duration of heating (hr.)	Ether recovered (g)	Yields of reaction products (%): thiol	Yields of reaction products (%): sulfide	Yields of reaction products (%): total	Amount of 1,2'-sulfide in sulfide fr. (%)	α-Addition of H_2S (%)
1	40.0	1.95	–	90	–	–	3.0	69.0	21.4	90.4	–	–
2	20.0	1.05	0.03	10	60 40	48 40	2.1	35.8	60.4	96.2	50.0	30
3	15.0	0.5	0.02	18	60 40	90 90	1.8	5.6	77.0	82.6	17.0	13

TABLE 10

Expt. No.	Amount taken: of ether (g)	Amount taken: of H_2S (moles per mole of ether)	Amount taken: of catalyst (ml)	Experimental conditions: total duration (days)	Experimental conditions: temp. at which heated (°C)	Experimental conditions: duration of heating (hr.)	Ether recovered (g)	Yields of reaction products (%): thiol	Yields of reaction products (%): sulfide	Yields of reaction products (%): total	Amount of 1,2'-sulfide in sulfide fr (%)	α-Addition of H_2S (%)
1	30.0	1.2	–	150	–	–	10.0	65.8	20.3	86.1	88.6	18
2	30.0	0.6	–	150	–	–	18.8	57.6	24.3	81.9	66.4	15
3	20.0	1.0	–	35	60	245	0.8	16.5	48.0	64.5	91.7	44
4	29.5	1.0	0.01	27	60	283	–	8.3	52.3	60.6	90.4	~50
5	24.0	0.9	0.02	12	60	63	–	19.7	37.4	57.1	104.4	~40
6	20.0	0.4	0.02	13	60	63	–	–	71.8	71.8	21.6	~15

SUMMARY

1. Reaction of hydrogen sulfide with ethyl, propyl, isopropyl, isobutyl, octyl, isopentyl, and cyclohexyl vinyl ethers yielded 2-alkoxyethanethiols and mixtures of sulfides containing various proportions of the isomeric dialkoxy diethyl sulfides. Addition products formed in violation of Markovnikov's rule predominated in the reaction mixtures, particularly in the case of ethers having normal alkyl radicals. Ethers having branched (isopentyl) and cyclic (cyclohexyl) radicals gave particularly high yields of "normal" addition products.

2. A general method is given for the synthesis of 2-alkoxyethanethiols $ROCH_2CH_2SH$ in 55-80% yield from the corresponding vinyl ethers.

3. It is suggested that the ratio of Markovnikov and anti-Markovnikov addition products is related to the tendency of the vinyl ether to react by an ionic mechanism.

Received February 10, 1952

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* See Consultants Bureau Translation, page 235.
** See Consultants Bureau Translation, page 453.
*** See Consultants Bureau Translation, page 325.
**** See Consultants Bureau Translation, page 459.

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NEW METHOD FOR THE SYNTHESIS OF AMINO PHOSPHONIC ACIDS

COMMUNICATION 2. REACTION OF KETONES WITH DIALKYL PHOSPHITES AND AMMONIA

T. Ya. Medved and M. I. Kabachnik

We have recently described a new method for the synthesis of aminoalkylphosphonic acids by reaction of aldehydes with dialkyl phosphites and ammonia [1]. We in fact found that, when dialkyl phosphites are heated with an alcoholic solution of ammonia and aldehydes, esters of the corresponding amino phosphonic acids are formed; hydrolysis of the esters then results in the formation of free amino phosphonic acids:

$$RCHO + NH_3 + HPO(OC_2H_5)_2 \rightarrow RCH(NH_2)PO(OC_2H_5)_2 + H_2O \xrightarrow{HCl,\ H_2O} RCH(NH_2)PO(OH)_2.$$

Owing to its simplicity, this synthesis has made possible the preparation of a number of substances hitherto inaccessible. In the preceding communication, we described the preparation of a number of aliphatic-aromatic amino phosphonic acids from aromatic aldehydes and diethyl or dibutyl phosphite, and also a number of experiments carried out with the object of elucidating the mechanism of the reaction. We showed that in presence of ammonia aldehydes react in the cold with dialkyl phosphites with formation of esters of hydroxyalkylphosphonic acids. Since this reaction was catalyzed also by hydroxyl ions [2], we considered that in our reaction, the ammonia acted as a basic catalyst:

$$NH_3 + HPO(OR)_2 \rightleftharpoons NH_4^+ + (RO)_2PO^-;$$

$$(RO)_2PO^- + RCHO \longrightarrow RCH(O^-)PO(OR)_2;$$

$$RCH(O^-)PO(OR)_2 + NH_4^+ \rightleftharpoons RCH(OH)PO(OR)_2 + NH_3.$$

When the reaction mixture was heated, the second stage of the reaction —replacement of the hydroxyl of the hydroxyalkylphosphonic ester by amino— took place:

$$NH_3 + R \cdot CH(OH)PO(OR)_2 \rightarrow RCH(NH_2)PO(OR)_2 + H_2O.$$

Great interest was presented by the possibility of extending the new reaction to ketones.

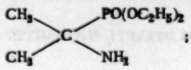
In the present investigation, we have shown that our reaction occurs also in the ketone series. Dialkyl phosphites react with ammonia and ketones much more readily than they do with ammonia and aldehydes. A shorter period of heating is required for the completion of the reaction, and in a number of cases heating in sealed tubes may be replaced by passage of ammonia into the heated reaction mixture. By the condensation of ketones with dialkyl phosphites and ammonia, amino phosphonic esters having a secondary carbon

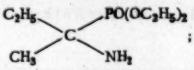
$$R_2CO + NH_3 + HPO(OC_2H_5)_2 = R_2C(NH_2)PO(OC_2H_5)_2 + H_2O$$

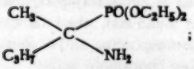
and the corresponding acids —substances that have previously been difficultly accessible— may now be prepared.

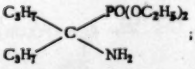
The reaction is applicable not only to aliphatic and alicyclic ketones, but also to aliphatic-aromatic and purely aromatic ketones. The aliphatic ketones react the most readily. Acetone, 2-butanone, 2-pentanone, and 4-heptanone will react with an equivalent amount of diethyl phosphite and 10% alcoholic ammonia when heated in sealed tubes in a boiling water bath for three hours. Practically the same results can be obtained by passing dry gaseous ammonia for 5-6 hours through a refluxed mixture of the ketone and diethyl phosphite. The products are the esters of 1-amino-1-methylethylphosphonic acid (I), 1-amino-1-methylpropylphosphonic acid (II), 1-amino-1-methylbutylphosphonic acid(III), and 1-amino-1-propylbutylphosphonic acid(IV). These products are obtained in yields of about 40%. They can be isolated from the reaction

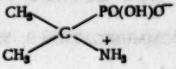
mixture either in the form of salts (picrates or hydrochlorides), or in the free state by vacuum distillation. When they are heated with diluted (1:1) hydrochloric acid in sealed tubes at 110-120°, the ester groups are hydrolyzed and the corresponding free amino phosphonic acids (V, VI, VII, and VIII) are formed:

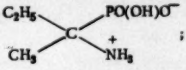
(I)  ;

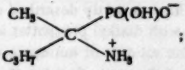
(II)  ;

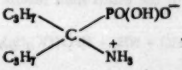
(III)  ;

(IV)  ;

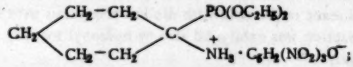
(V)  ;

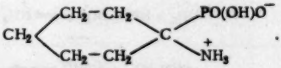
(VI)  ;

(VII)  ;

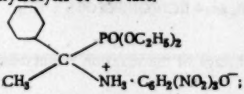
(VIII)  .

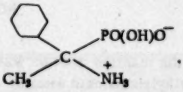
Alicyclic and aliphatic-aromatic ketones react with greater difficulty. Thus, cyclohexanone under the same conditions, but heated in the sealed tube for seven hours, forms the corresponding ester of 1-aminocyclohexylphosphonic acid, which was isolated as the picrate (IX); from the latter the free amino phosphonic acid (X) was obtained:

(IX)  ;

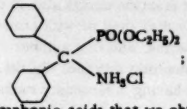
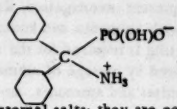
(X)  .

Reaction with acetophenone also requires longer heating; it yields the ester of 1-amino-1-phenylethylphosphonic acid in 20-25% yield. We again isolated this as the picrate (XI) and obtained the free amino phosphonic acid (XII) by the hydrolysis of this salt:

(XI)  ;

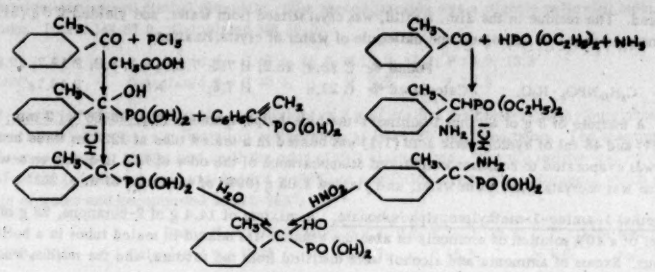
(XII)  .

Benzophenone was the least ready to react. Treatment of the reaction mixture gave the hydrochloride of aminodiphenylmethylphosphonic ester (XIII) in a yield of only 13%. The free aminodiphenylmethylphosphonic acid (XIV) was prepared by heating the hydrochloride with hydrochloric acid:

(XIII)  ; (XIV)  .

All of the free amino phosphonic acids that we obtained are actually internal salts; they are colorless high-melting crystalline substances, and crystallize from water with one or two molecules of water of crystallization. The amino group of an amino phosphonic acid can readily be converted into a hydroxyl group by the action of nitrous acid. We generally determined the amino nitrogen in the synthesized compounds by the Van Slyke method.

We converted our 1-amino-1-phenylethylphosphonic acid (XII) into 1-hydroxy-1-phenylethylphosphonic acid by the action of nitrous acid in aqueous solution. The latter compound has been prepared previously by Conant [3] from benzaldehyde and phosphorus trichloride; the mixture of hydroxy acid and unsaturated acid at first formed was converted by Conant into the chloro acid by the action of hydrogen chloride, and this was isolated in the pure state and then carefully hydrolyzed to the hydroxy acid. We repeated this synthesis and obtained 1-hydroxy-1-phenylethylphosphonic acid. Comparison of the two specimens of hydroxy acid obtained by different methods showed them to be identical:



Both specimens melted at 149°, and a mixture test showed no depression. The analyses also gave confirmation of the identity of the two substances. The structure of the amino acid and the general scheme of our reaction are confirmed by this preparation of a hydroxy acid of known structure from our amino acid.

EXPERIMENTAL

Diethyl 1-amino-1-methylethylphosphonate. 1) A mixture of 15 g of acetone, 35 g of diethyl phosphite, and 75 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for three hours. Excess of alcohol and ammonia was distilled from the reaction mixture, and the residue was vacuum-distilled. After two fractionations, two fractions were obtained:

Fraction I, b.p. 45-46° (3 mm); n_D^{20} 1.4062; d_4^{20} 1.0676; 3.1 g

Fraction II, b.p. 65-66° (3 mm); n_D^{20} 1.4327; d_4^{20} 1.0437; 24.3 g

The first fraction was found to be impure unchanged diethyl phosphite. The second fraction, a light-yellow liquid, was diethyl 1-amino-1-methylethylphosphonate, obtained in 47.5% yield. Found MR 48.5. Calculated MR 48.8.

Found %: C 43.1; 43.0; H 9.7; 9.5; P 15.6; 15.9; N 7.5; 7.6

$C_7H_{18}NPO_3$. Calculated %: C 43.1; H 9.2; P 15.9; N 7.2

2) A mixture of 12 g of acetone and 28 g of diethyl phosphite was placed in a three-necked flask fitted with reflux condenser, thermometer, and tube for passage of gas. Dry ammonia was passed through the mixture, and the temperature rose to 48°. When the temperature had fallen again, the mixture was heated for three hours in a water bath at 50°, and then for two hours in a boiling water bath. The reaction mixture was vacuum-distilled. After two distillations, two fractions were obtained:

Fraction I, b.p. 62-67° (4 mm); n_D^{20} 1.4063; 2.8 g

Fraction II, b.p. 66-67° (3 mm); n_D^{20} 1.4333; d_4^{20} 1.0432; 17.0 g

Yield 42.5%. Found MR 48.6. Calculated MR 48.8.

Picrate of diethyl 1-amino-1-methylethylphosphonate. A mixture of 3 g of acetone, 7 g of diethyl phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for three hours. The reaction mixture was then evaporated down in a porcelain dish on a boiling water bath until a constant residue was obtained. The syrupy yellow residue was dissolved in 20 ml of ethanol, and an ethereal solution of picric acid was added. The picrate was recrystallized from absolute ethanol; 8.7 g (40%) was obtained, m.p. 175°.

Found %: C 36.9; 37.1; H 4.7; 4.9; N 13.5; 13.2; P 7.1; 7.2

$C_{13}H_{21}N_4PO_{10}$. Calculated %: C 36.8; H 4.9; N 13.2; P 7.3

1-Amino-1-methylethylphosphonic acid. 1) A mixture of 2 g of the picrate of diethyl 1-amino-1-methylethylphosphonate, m.p. 175°, and 40 ml of hydrochloric acid (1:1) was heated in sealed tubes at 120-125° for three hours. Then, in order to remove picric acid, the contents of the tubes were extracted with ether until the aqueous layer was decolorized. The aqueous layer was evaporated on a boiling water bath until the odor of HCl

disappeared. The residue in the dish, a solid, was crystallized from water, and yielded 0.6 g (91%) of a colorless crystalline substance. It contained one molecule of water of crystallization.

Found %: C 23.4; 23.2; H 7.5; 7.5; N 9.1; 8.9; P 19.7; 19.8; H_2O 11.7

$C_3H_{10}NPO_3 \cdot H_2O$. Calculated %: C 22.9 H 7.6; N 8.9; P 19.7; H_2O 11.5

2) A mixture of 3 g of diethyl 1-amino-1-methylethylphosphonate (b.p. 65-66° at 3 mm; n_D^{20} 1.4327; d_4^{20} 1.0437) and 45 ml of hydrochloric acid (1:1) was heated in a sealed tube at 120° for three hours. The reaction mixture was evaporated to constant weight and disappearance of the odor of HCl in a dish on a water bath. The dry residue was recrystallized from water, and yielded 1.95 g (90%) of substance of m.p. 258°.

Diethyl 1-amino-1-methylpropylphosphonate. A mixture of 14.4 g of 2-butanone, 28 g of diethyl phosphite, and 60 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for three hours. Excess of ammonia and alcohol were distilled from the mixture, and the residue was vacuum-distilled. After two distillations the following fractions were obtained:

Fraction I, b.p. 42-45° (3 mm); n_D^{20} 1.4069; 4.8 g

Fraction II, b.p. 87-88° (5 mm); n_D^{20} 1.4397; d_4^{20} 1.0381; 15.1 g

The first fraction was found to be impure unchanged diethyl phosphite. The second fraction, a light-yellow liquid, was diethyl 1-amino-1-methylpropylphosphonate, obtained in 36% yield. Found MR 53.1. Calculated MR 53.4

Found %: N 6.2; P 14.7; 14.8; C 46.2; 46.2; H 9.7; 9.7

$C_6H_{16}NPO_3$. Calculated %: N 6.7; P 14.8; C 45.9; H 9.6

Picrate of diethyl 1-amino-1-methylpropylphosphonate. A mixture of 3.6 g of 2-butanone, 7 g of diethyl phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for three hours. The reaction mixture was then evaporated in a porcelain dish on a boiling water bath to constant weight. The yellow syrupy residue was dissolved in 20 ml of ethanol, and an ethereal solution of picric acid was added until precipitation of the picrate was complete. The picrate was filtered off and recrystallized from absolute ethanol, yielding 6.2 g (28%) of a yellow crystalline substance, m.p. 166°.

Found %: N 13.3; 13.2; P 7.1; 7.3

$C_{14}H_{23}N_4PO_{10}$. Calculated %: N 13.2; P 7.1

1-Amino-1-methylpropylphosphonic acid. 1) A mixture of 3 g of diethyl 1-amino-1-methylpropylphosphonate and 40 ml of hydrochloric acid (1:1) was heated in sealed tubes at 120° for three hours. The reaction mixture was evaporated to constant weight and disappearance of the odor of HCl on a boiling water bath. The dry residue was recrystallized from a mixture of water and alcohol, and yielded 1.4 g (57%) of a colorless crystalline substance, which decomposed at 262°. It crystallized with one molecule of water.

Found %: P 18.1; 18.2; N 8.3; 8.3; H_2O 10.7

$C_4H_{12}NPO_3 \cdot H_2O$. Calculated %: P 18.1; N 8.2 H_2O 10.5

2) A mixture of 2 g of the picrate of diethyl 1-amino-1-methylpropylphosphonate (m.p. 166°) and 40 ml of hydrochloric acid (1:1) was heated in sealed tubes at 120-130° for three hours. The contents of the tubes were extracted with water until the water layer was decolorized. The water layer was evaporated on a boiling water bath until the odor of HCl disappeared. The solid residue in the dish was recrystallized from water, and yielded 0.45 g (65%) of a colorless crystalline substance, m.p. 262°.

Found %: P 18.2; 18.2; N 7.9; 7.9; H_2O 10.3

$C_4H_{12}NPO_3 \cdot H_2O$ Calculated %: P 18.1; N 8.2; H_2O 10.5

Diethyl 1-amino-1-methylbutylphosphonate. A mixture of 4.3 g of 2-pentanone, 7 g of diethyl phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol was heated for three hours in a boiling water bath. The reaction mixture was vacuum-fractionated. Two distillations yielded the following fractions:

Fraction I, b.p. 36-40° (2 mm); n_D^{20} 1.4065; 6.1 g

Fraction II, b.p. 82-83° (2 mm); n_D^{20} 1.4400; d_4^{20} 1.0320; 16.4 g

Yield 32.2%.

The first fraction was impure diethyl phosphite. The second fraction was a slightly yellowish mobile liquid having a feeble odor. Found MR 57.0. Calculated MR 58.0.

	Found %:	C 48.3; 48.2; H 10.2; 10.1; P 14.0; 13.9
$C_8H_{22}NPO_3$.	Calculated %:	C 48.4; H 9.9; P 13.9

1-Amino-1-methylbutylphosphonic acid. A mixture of 3 g of diethyl 1-amino-1-methylbutylphosphonate and 60 ml of hydrochloric acid (1:1) was heated in sealed tubes at 120-130° for three hours. The reaction mixture was evaporated down to constant weight and until the odor of HCl disappeared. The dry residue was recrystallized from a mixture of water and alcohol, and yielded 1.4 g (56%) of a colorless crystalline substance, which crystallized with one molecule of water and decomposed at 262-263°.

	Found %:	C 32.4; 32.4; H 9.1; 9.2; P 16.8; 16.9; N 7.7; 7.6; H_2O 9.95
$C_5H_{14}NPO_3 \cdot H_2O$	Calculated %:	C 32.4; H 8.7; P 16.8; N 7.6; H_2O 9.73

Diethyl 1-amino-1-propylbutylphosphonate. Dry ammonia was passed for one hour at room temperature into a mixture of 11.4 g of 4-heptanone (b.p. 142-144°; n_D^{20} 1.4045) and 14 g of diethyl phosphite; no rise of temperature was observed. The reaction mixture was then heated in a water bath at 50° for three hours, and then for two hours in a boiling water bath. On cooling, the reaction mixture partially crystallized out. The crystals were filtered off and washed with dry ether (3.8 g of a colorless crystalline substance, m.p. 95°). The substance was an ammonium salt, for treatment with alkali resulted in the immediate evolution of ammonia. The analysis corresponded to the ammonium salt of monoethyl phosphite:

	Found %:	C 19.3; 19.3; H 7.8; 7.9; P 24.8; 24.7
$C_2H_{10}NPO_3$.	Calculated %:	C 18.9; H 7.8; P 24.4

The filtrate from the separation of the crystals was vacuum-fractionated, and after two distillations 8.2 g (33%) of a fraction of b.p. 106-108° at 3 mm was isolated: n_D^{20} 1.4447; d_4^{20} 1.0034. Found MR 66.54. Calculated MR 67.2.

	Found %:	C 52.5; 52.8; H 10.4; 10.5; P 12.4; 12.3; N 6.0; 6.1
$C_{11}H_{26}NPO_3$.	Calculated %:	C 52.6; H 10.4; P 12.4; N 5.6

1-Amino-1-propylbutylphosphonic acid. A mixture of 4 g of the ethyl ester obtained in the preceding experiment and 60 ml of hydrochloric acid (1:1) was heated in a sealed tube at 120° for three hours. The reaction mixture was evaporated to constant weight and disappearance of the odor of HCl on a boiling water bath. The syrupy residue was dried for several days in a desiccator over phosphoric anhydride, and it then crystallized out. It was recrystallized from a mixture of absolute ethanol and ethyl acetate. The product was 2.1 g of colorless crystals, m.p. 192°.

Picrate of diethyl 1-aminocyclohexylphosphonate. A mixture of 5.7 g of cyclohexanone, 8 g of diethyl phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for seven hours. The reaction mixture was then evaporated in a dish to constant weight in a boiling water bath. The syrupy residue was dissolved in 20 ml of ethanol, and an ethereal solution of picric acid was added until precipitation was complete. Recrystallization of the precipitate from absolute ethanol yielded 5.6 g (19%) of substance, m.p. 172°.

	Found %:	C 41.4; 41.5; H 5.7; 5.4; N 12.2; 12.3; P 6.8; 6.9
$C_{18}H_{25}N_4O_{10}P$.	Calculated %:	C 41.4; H 5.4 N 12.1; P 6.7

1-Aminocyclohexylphosphonic acid. A mixture of 1 g of the picrate of diethyl 1-aminocyclohexylphosphonate and 20 ml of hydrochloric acid (1:1) was heated in a sealed tube at 120-130° for three hours. The contents of the tubes were then extracted with ether until the aqueous layer was decolorized. The aqueous layer was evaporated on a water bath until the odor of HCl disappeared. The solid remaining in the dish was recrystallized from water, and yielded 0.35 g (91%) of colorless crystals, m.p. 238°. The substance crystallized with one molecule of water.

	Found %:	C 36.8; 36.5; H 7.8; 7.9; N 6.9; 7.0; P 15.6; 15.4; H_2O 9.16
$C_6H_{14}NPO_3 \cdot H_2O$.	Calculated %:	C 36.5; H 8.1; N 7.1; P 15.7; H_2O 9.15

After being dried at 150°, the substance was again analyzed:

	Found %:	C 40.1; 40.2; H 7.7; 7.6
$C_6H_{14}NPO_3$.	Calculated %:	C 40.2; H 7.8

Picrate of diethyl 1-amino-1-phenylethylphosphonate. A mixture of 12 g of acetophenone, 14 g of diethyl phosphite, and 25 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for seven hours. Excess of alcohol and ammonia was removed under reduced pressure. The residue was dissolved in dry ether (20-30 ml), and an ethereal solution of picric acid was added. The precipitated picrate was recrystallized from absolute ethanol; 16.2 g (33%), m.p. 174-175°, was obtained.

	Found %:	N 11.4; 11.2; P 6.1; 6.4
$C_{18}H_{23}N_4PO_{10}$.	Calculated %:	N 11.5; P 6.4

1-Amino-1-phenylethylphosphonic acid. A mixture of 7 g of the picrate of diethyl 1-amino-1-phenylethylphosphonate and 140 ml of hydrochloric acid (1:1) was heated in sealed tubes for three hours at 130-135°. The contents of the tubes were extracted with ether until the aqueous layer was decolorized. The aqueous layer was evaporated on a boiling water bath until the odor of HCl completely disappeared. The solid residue was recrystallized from water (it was dissolved in about 700 ml of water after long boiling, and the solution was then evaporated to one-tenth of its original volume). The product was 2.65 g (81%) of a slightly yellowish crystalline substance, m.p. 235°; it crystallized with one molecule of water.

	Found %:	P 14.6; 14.4; N 6.4; 6.5; H_2O 8.3
$C_8H_{12}NPO_3 \cdot H_2O$	Calculated %:	P 14.2; N 6.4; H_2O 8.2

Reaction of 1-amino-1-phenylethylphosphonic acid with nitrous acid. Nitrogen oxides were passed through an ice-cooled solution of 1 g of 1-amino-1-phenylethylphosphonic acid in 500 ml of water. Several minutes after passage of the gas, bubbles of gas began to separate throughout the whole liquid. Nitrogen oxides were passed for four hours, until formation of gas bubbles stopped completely. Toward the end of the reaction the solution was heated to 50° for 30 minutes. The solution was then evaporated under reduced pressure, the bath temperature not exceeding 40-50°. The syrupy residue was dried in a vacuum desiccator over calcium chloride and caustic potash. It then crystallized out, and was recrystallized from a mixture of dry ether and chloroform. After a few recrystallizations it melted at 149°. A mixture melting point with 1-hydroxy-1-phenylethylphosphonic acid prepared by Conant's method [3] (m.p. 150°) showed no depression.

	Found %:	C 47.8; 47.7; H 5.8; 5.5; P 15.7; 15.3
$C_8H_{11}PO_4$.	Calculated %:	C 47.5; H 5.5; P 15.3

Hydrochloride of diethyl aminodiphenylmethylphosphonate. A mixture of 13.5 g of benzophenone, 10 g of diethyl phosphite, and 23 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for seven hours. The contents of the tubes were then evaporated to constant weight on a boiling water bath. The residue consisted of two liquid layers, which readily solidified on standing; they were separated and treated separately. The lower layer was found to be a mixture of ammonium salts of phosphorus acids, and it was not investigated further. The upper layer was dissolved in dry ether, and into the solution, cooled with ice water, hydrogen chloride was passed. The ether and excess of hydrogen chloride was removed under reduced pressure at room temperature, the ether that distilled off being periodically replaced by fresh ether to bring the volume to its initial value. After removal of hydrogen chloride, the ether solution yielded colorless crystals of the hydrochloride, and the unchanged benzophenone remained in the ether. The crystals were filtered off, washed with ether, and recrystallized from a mixture of ether and alcohol, yielding 3.5 g (13%) of a colorless crystalline substance, m.p. 144°.

	Found %:	N 4.4; 4.5; P 8.3; 8.0
$C_{17}H_{23}O_3NPCl$.	Calculated %:	N 3.9; P 8.7

Aminodiphenylmethylphosphonic acid. A mixture of 1.8 g of the hydrochloride of diethyl aminodiphenylmethylphosphonate and 36 ml of hydrochloric acid (1:1) was heated in sealed tubes at 110-120° for three hours. The contents of the tubes were then evaporated on a boiling water bath until the odor of HCl completely disappeared. The residue was recrystallized from aqueous alcohol, and yielded 1.2 g (90%) of a colorless crystalline substance, m.p. 232°; it crystallized with two molecules of water.

	Found %:	N 4.9; 4.9; P 10.5; 10.3; H_2O 11.8
$C_{13}H_{14}PNO_3 \cdot 2H_2O$.	Calculated %:	N 4.7; P 10.4; H_2O 12.0

SUMMARY

1. It has been shown that our condensation reaction between dialkyl phosphites, aldehydes, and ammonia can be extended also to ketones. The reaction can be applied not only to aliphatic and alicyclic ketones, but also to aliphatic-aromatic and purely aromatic ketones. The reaction of dialkyl phosphites with ammonia and

ketones results in the formation of esters of α-amino phosphonic acids having a branched radical.

2. A simple method has been developed for the preparation of amino phosphonic acids by the action of ketones on dialkyl phosphites and ammonia, and hydrolysis of the esters so formed.

3. The following substances have been synthesized and characterized: 1-amino-1-methylethylphosphonic acid, 1-amino-1-methylpropylphosphonic acid, 1-amino-1-methylbutylphosphonic acid, 1-amino-1-propylbutylphosphonic acid, 1-aminocyclohexylphosphonic acid, 1-amino-1-phenylethylphosphonic acid, and aminodiphenylmethylphosphonic acid, and also their esters, and the hydrochlorides and picrates of these esters.

Received December 23, 1952

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SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

COMMUNICATION 4. COPOLYMERIZATION OF 2-VINYLOXYETHYLAMINE WITH METHYL METHACRYLATE

M. F. Shostakovsky, I. A. Chekulaeva, and A. M. Khomutov

We have pointed out in previous communications [1, 2, 3] that 2-vinyloxyethylamine $CH_2=CHOCH_2CH_2NH_2$ differs from alkyl vinyl ethers in chemical properties: it has a considerably lower tendency to undergo reactions that proceed by an ionic mechanism. This behavior of 2-vinyloxyethylamine is to be explained by the association in its molecule of the double bond with two centers capable of forming onium compounds (O and N), and also by the possibility of the formation of a hydrogen bond [3].

In order to extend our ideas concerning the properties of 2-vinyloxyethylamine, in the present investigation, we have studied its behavior in polymerization and copolymerization reactions proceeding by a free-radical mechanism. Investigations in this direction have been made for alkyl vinyl ethers [4, 5, 6], but there have been none at all for vinyl ethers containing functional groups (NH_2 or OH).

Experiments on the polymerization of 2-vinyloxyethylamine showed that, as in the case of alkyl vinyl ethers [4, 5], polymerization could not be induced by benzoyl peroxide. Hence, a component was selected for copolymerization with 2-vinyloxyethylamine which is known to react by a free-radical mechanism in presence of benzoyl peroxide and could draw the double bond of the vinyl ether into the process. As a result of this investigation, the copolymerization of 2-vinyloxyethylamine with methyl methacrylate was effected (Tables 1 and 2). The copolymers obtained contained various proportions of 2-vinyloxyethylamine, and these increased as the concentration of the vinyl ether in the original mixture was increased.

TABLE 1

Expt. No.	Molar ratio of vinyl ether to methyl methacrylate	Yield of reaction products		Extent to which methyl methacrylate participated in copolymerization (%)
		copolymer (% of total amount	addition product (% of theoretical)	
1	0:1	94	—	94.0
2	1:19	6	74.5	6.3
3	1:3	24	50.5	29.9
4	1:1	34	44.1	57.0
5	3:1	18	50.0	50.5
6	19:1	4	55.5	54.5
7	1:0	Does not polymerize	—	—

On the basis of considerations that we have advanced previously [4], the mechanism of the copolymerization process can be visualized as follows: the benzoyl peroxide initiates a molecule of methyl methacrylate with formation of an active radical, which then draws the double bond of the 2-vinyloxyethylamine into the chain reaction. This is confirmed by the absence of polymerization in pure 2-vinyloxyethylamine in presence of benzoyl peroxide under these conditions; methyl methacrylate, on the other hand, owing to the presence of conjugated bonds $-C=C-C=O$, is very active in these processes.

Nevertheless, it must be emphasized that in the present case, no methyl methacrylate polymer was found among the reaction products. It has thus been shown that copolymerization is not accompanied by formation of the polymer of the initially active component. It has been established, however, that reaction of 2-vinyloxyethylamine with methyl methacrylate proceeds not only with formation of copolymers, but with formation also of the methyl ester of 2-methyl-3-(2-vinyloxyethylamino) propionic acid in accordance with the equation:

$$CH_2=CHOCH_2CH_2NH_2 + CH_2=C(CH_3)COOCH_3 \rightarrow CH_2=CHOCH_2CH_2NHCH_2CH(CH_3)COOCH_3.$$

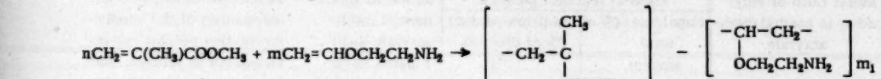
TABLE 2

Expt. No.	Molar ratio of vinyl ether to methyl methacrylate	Nitrogen content of copolymer (%)	Molar content of vinyl ether in copolymer (%)	Molar ratio of vinyl ether to methyl methacrylate in copolymer	Relative viscosity η_{rel}	Description of polymer or copolymer
1	0:1	–	–	0:1	3.61	Colorless, hard, brittle, soluble in acetone
2	1:19	0.25	1.8	1:55	1.297	The same
3	1:3	0.5 0.6	3.9	1:24.5	2.54	The same
4	1:1	1.77 1.73	12.4	1:7.0	–	Colorless, hard, insoluble in usual solvents; does not melt
5	3:1	4.30 4.11	29.0	1:2.5	–	Yellow, hard, insoluble in usual solvents
6	19:1	5.07 5.33	35.7	1:2.0	–	The same

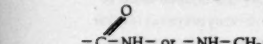
It has been shown that benzoyl peroxide is without effect on the course of this reaction: methyl 2-methyl-3-(2-vinyloxyethylamino) propionate is formed in the same yield, both in presence and absence of benzoyl peroxide. Under the given conditions the yield of product depends on the ratio of the original components: it increases with increase in the excess of methyl methacrylate (Table 3).

Investigation of the properties of methyl 2-methyl-3-(2-vinyloxyethylamino)propionate has shown that under the given conditions it not only does not polymerize in presence of benzoyl peroxide, but also does not copolymerize with methyl methacrylate. The possibility of this product being involved in the chain polymerization reaction is, therefore, apparently excluded.

Hence, in the initial stage, the formation of copolymers can be represented as follows:



Cross-linking with formation of a three-dimensional structure then follows, and infusible, insoluble copolymers result. In the present case, the cross-linking of the macromolecules may proceed with the participation of the functional groups NH_2, $COOCH_3$, and $CH_2=C(CH_3)$, leading to the formation of linkages of the type



This is confirmed by 1) the fact that methyl 2-methyl-3-(2-vinyloxyethylamino)propionate is formed, and 2) data in the literature on the reactions of acrylic acid derivatives with amines [7-10].

EXPERIMENTAL

A. Starting materials. 2-Vinyloxyethylamine was purified by treatment with sodium followed by distillation: b.p. 115-117°; n_D^{20} 1.4390. The methyl methacrylate used had the following constants: b.p. 34.5° (55 mm); n_D^{20} 1.4150. The benzoyl peroxide was purified by being precipitated twice from chloroform solution with methanol; it contained 99.1% of the peroxide.

B. Experimental procedure. Copolymerization was carried out in glass tubes, which were heated in a thermostat at 60-62°. The starting materials (5 g in all) were taken in various molar ratios, and 0.01 g of benzoyl peroxide was added (0.2% on the total amount of monomers). The process was continuous over 100 hours. Under the same conditions two control experiments were performed on the polymerization in presence of benzoyl peroxide of pure methyl methacrylate and pure 2-vinyloxyethylamine. The treatment of the reaction products was determined by their properties.

I. Copolymerization of 2-Vinyloxyethylamine and Methyl Methacrylate

a) Copolymerization at a molar ratio of 2-vinyloxyethylamine to methyl methacrylate of 1:19. At the end of 100 hours, the mixture obtained from 0.22 g of 2-vinyloxyethylamine and 4.67 g of methyl methacrylate remained liquid; 4.9 g of it was vacuum distilled and yielded the following fractions:

Fraction I, b.p. 18° (10 mm); n_D^{20} 1.4155; 3.9 g

Fraction II, viscous residue 1.0 g

4.9 g

Fraction I was methyl methacrylate. Fraction II was dissolved in acetone, from which it was precipitated as a white solid by means of methanol; this solid was separated from the main solution and vacuum-dried at 20°, yielding 0.3 g of a hard brittle colorless polymer. For the purpose of analysis, it was twice precipitated from acetone solution with methanol.

Found %: C 59.89; 59.64; H 8.37; 8.18; N 0.25

The analysis corresponded to a copolymer containing traces of nitrogen.

The acetone-methanol solution was vacuum-distilled, and yielded:

Fraction I, b.p. 120-125° (20 mm); n_D^{17} 1.4499; 0.35 g

Fraction II, resin 0.05 g

0.40 g

Fraction I was methyl 2-methyl-3-(2-vinyloxyethylamino)propionate. The detailed investigation of this fraction is given in g) (below).

b) Copolymerization at a molar ratio of 2-vinyloxyethylamine to methyl methacrylate of 19:1. Throughout the whole course of the polymerization process the reaction mixture remained liquid. Its treatment was carried out as in the preceding experiment, with the exception that the copolymer was purified not by the precipitation method, but by repeated washing with acetone. No methyl methacrylate polymer could be detected in the acetone washings.

c) Copolymerization at a molar ratio of 2-vinyloxyethylamine to methyl methacrylate of 1:3. Thirty hours after the commencement of the heating of 1.12 g of 2-vinyloxyethylamine with 3.88 g of methyl methacrylate, a rise in viscosity was observed. Toward the end of the process the reaction product became very thick, but was still fluid. It was dissolved in acetone, from which it was precipitated by methanol as a hard, brittle, colorless polymer (1.2 g). Before analysis, the polymer was washed repeatedly with methanol.

Found %: C 59.98; 59.99; H 8.20; 8.22; N 0.5; 0.6

The analysis corresponded to a copolymer containing 3.9 mole-% of the vinyl ether.

Vacuum distillation of the alcohol-acetone solution yielded:

Fraction I, b.p. 125-130° (25 mm); n_D^{20} 1.4491; 1.3 g

Fraction II, resin 0.1 g

1.4 g

The investigation of Fraction I, which was methyl 2-methyl-3-(2-vinyloxyethylamino)propionate, is described under g).

d) Copolymerization at a molar ratio of 2-vinyloxyethylamine to methyl methacrylate of 3:1. During the polymerization process the viscosity varied as in c). The product, however, was insoluble in most solvents (acetone, ether, benzene, alcohols, water, dioxane, vinyl ethers, chloroform, etc.) and was, therefore, purified by repeated washing with acetone and ether. No methyl methacrylate polymer was isolated from the acetone-ether mixture.

e) Copolymerization at a molar ratio of 2-vinyloxyethylamine to methyl methacrylate of 1:1. Polymerization began after six hours, and attained a maximum after 43 hours. The reaction product was a jellylike substance and was treated as in d). No methyl methacrylate polymer was obtained.

f) Polymerization of pure methyl methacrylate. Under the conditions described under B, methyl methacrylate polymerized to a solid in six hours, but it was kept in the thermostat for 100 hours in order to give comparable results. The product was dissolved in acetone, from which it was precipitated by methanol as a hard, brittle, colorless polymer.

The results of all of the copolymerization experiments are given in Tables 1 and 2.

g) Investigation of the product accompanying the copolymer. The product was collected from all of the experiments on the copolymerization of 2-vinyloxyethylamine and methyl methacrylate, and was vacuum-distilled. In its analysis it corresponded to the compound:

$$CH_2=CHOCH_2CH_2NHCH_2-CH(CH_3)COOCH_3.$$

It was a colorless liquid, soluble in benzene, ether, acetone, and methanol, having b.p. 97.5° (4 mm); n_D^{20} 1.4491; d_4^{20} 0.9998; calculated for $C_9H_{17}O_3N$ MR 50.19; found MR 50.24; found (cryoscopically in benzene) M 182.0; 178.2; calculated for $C_9H_{17}O_3N$ M 187.2.

	Found %:	C 57.75; 57.97; H 9.27; 9.19; N 7.51; 7.61
$C_9H_{17}O_3N$.	Calculated %:	C 57.80; H 9.12; N 7.50

Hydrogenation of the product over Raney nickel at 50° in an autoclave yielded methyl 3-(2-ethoxyethylamino)-2-methylpropionate: b.p. 82° (2 mm); n_D^{20} 1.4333; d_4^{20} 0.9668; MR 50.88; calculated for $C_9H_{19}O_3N$ MR 50.54.

	Found %:	C 57.25; 56.99; H 10.24; 10.10; N 7.47; 7.45
$C_9H_{19}O_3N$.	Calculated %:	C 57.26; H 10.12; N 7.40

Other facts confirming the structure of the product are:

1. The ease and completeness of its hydrolysis by 2% sulfuric acid, which indicates presence of a vinyl group. The acetaldehyde formed in this way was determined iodometrically [11], giving, for the content of the compound, 96.3, 96.9%.

2. A negative reaction for the $-\overset{\overset{O}{\|}}{C}-NH-$ grouping, which would be present if the compound formed in the reaction was

$$CH_2=\underset{\underset{CH_3}{|}}{C}-\overset{\overset{O}{\|}}{C}-NHCH_2CH_2OCH=CH_2.$$

3. The compound did not polymerize in presence of benzoyl peroxide, which indicates the absence of a double bond capable of entering into polymerization by a radical mechanism under the given conditions.

4. The participation of the amino group of 2-vinyloxyethylamine in the formation of the compound under consideration was confirmed by the fact that N,N-diethyl-2-vinyloxyethylamine $(C_2H_5)_2NCH_2CH_2OCH=CH_2$ did not yield a similar compound with methyl methacrylate.

II. Reaction of 2-Vinyloxyethylamine with Methyl Methacrylate when Heated in Absence of Benzoyl Peroxide

A mixture of 2.33 g of 2-vinyloxyethylamine and 2.67 g of methyl methacrylate was heated in a thermostat under the conditions described under B. The reaction product was vacuum distilled, and yielded:

Fraction I, b.p. 27-32° (29 mm); n_D^{20} 1.4256;	2.7 g
Fraction II, b.p. 132.5° (24 mm); n_D^{20} 1.4493;	2.2 g
Fraction III, resin	0.05 g
	4.95 g

Fraction I was a mixture of the starting materials. Fraction II corresponded to the addition product formed by 2-vinyloxyethylamine and methyl methacrylate:

$$CH_2=CH-OCH_2CH_2NH-CH_2-CH(CH_3)COOCH_3.$$

Experiments were carried out in similar fashion in which molar ratios of vinyl ether to methyl methacrylate of 1:19 and 19:1 were used. The results are given in Table 3.

TABLE 3

Expt. No.	Molar ratio of 2-vinyloxyethylamine to methyl methacrylate	Yield of addition product (% of theoretical)
1	1:19	85.2
2	1:1	43.2
3	19:1	59.3

SUMMARY

1. It has been shown that pure 2-vinyloxyethylamine does not polymerize in presence of benzoyl peroxide under the conditions used.

2. The copolymerization of 2-vinyloxyethylamine and methyl methacrylate has been effected in presence of benzoyl peroxide.

3. It has been shown that, together with copolymerization, the formation of a new substance, methyl 2-methyl-3-(2-vinyloxyethylamino)propionate, occurs.

4. It has been pointed out that, in the course of the formation of the macromolecular compounds, not only double bonds, but also other functional groups of the original components, take part in the reaction.

5. Polymers of methyl methacrylate were absent in the reaction products.

Received November 29, 1952

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STEROCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 3. cis- AND trans-4-CYCLOHEXENE-1,2-DICARBOXYLIC ACIDS, AND THEIR REACTIONS

I. N. Nazarov and V. F. Kucherov

When Diels and Alder in 1928 prepared cis-4-cyclohexene-1,2-dicarboxylic acid by the condensation of maleic anhydride with 1,3-butadiene [1], it became clear that the structures of various cyclohexene-1,2-dicarboxylic acids and their derivatives, described previously by Bayer [2], did not correspond to the formulas ascribed to them. This is particularly true of the compounds of the trans series.

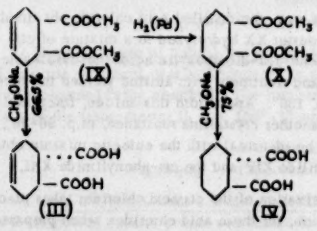
It was not till 1948 that Korolev and Mur [3] described for the first time the preparation of trans-4-cyclohexene-1,2-dicarboxylic acid by the condensation of 1,3-butadiene with fumaric acid and its acid chloride in boiling acetic acid. Shortly afterwards Alder and Schumacher [4], while studying the stereochemistry of the diene synthesis, also obtained this trans-acid and cleared up the question of the structures of various cyclohexene-1,2-dicarboxylic acids obtained by Bayer from the reduction of phthalic acid [2]. Quite recently, trans-4-cyclohexene-1,2-dicarboxylic acid has been prepared in 55% yield by heating 1,3-butadiene with fumaric acid in aqueous solution at 135° [5].

Having developed a convenient method for the synthesis of cyclic trans-1,2-dicarboxylic acids by the condensation of dienes with trans-dienophiles [6], we have now applied it in the preparation of trans-4-cyclohexene-1,2-dicarboxylic acid (III) and its derivatives with the object of studying the stereochemical transformations in this series.

When a mixture of dimethyl fumarate and 5-6 molecular proportions of 1,3-butadiene was heated in benzene at 200-205°, a 95% yield (calculated on the fumaric ester) was obtained of the dimethyl ester of trans-4-cyclohexene-1,2-dicarboxylic acid (I), and this gave a dibromide of m.p. 85-86° which differed from that described by Bayer [2]. Hydrolysis of the trans-diester I readily gave the known trans-4-cyclohexene-1,2-dicarboxylic acid (III), m.p. 171-172°, and hydrogenation of the ester gave the saturated trans-diester II, readily hydrolyzable to the known trans-1,2-cyclohexanedicarboxylic acid (IV).

When the trans-acid III was heated with excess of acetyl chloride, the trans-anhydride V, m.p. 186-187°, described by Alder and Schumacher [4], was readily obtained, and this, when hydrogenated in chloroform in presence of a Pd catalyst, gave the saturated trans-anhydride VI, m.p. 145-146°, which could be readily prepared also by the action of acetyl chloride on the saturated trans-acid IV. Boiling of the trans-anhydride V in absolute methanol solution yielded the trans-monoester VII in quantitative yield, and this, on hydrogenation, gave the known saturated trans-monoester VIII, m.p. 96° [7].

The trans-acids III and IV can be readily prepared also by the isomerization and hydrolysis with sodium methoxide of the corresponding cis-diesters IX and X, which we prepared by the action of diazomethane on cis-4-cyclohexene-1,2-dicarboxylic acid and cis-1,2-cyclohexanedicarboxylic acid respectively:

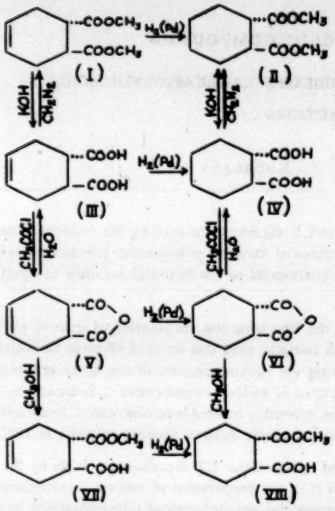


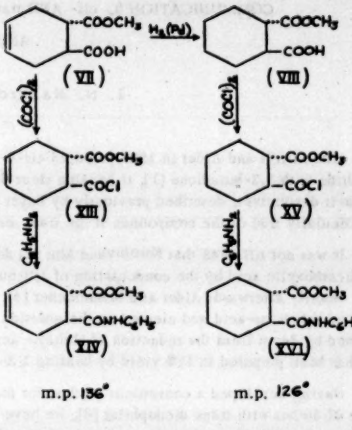
When the trans-anhydrides V and VI were heated at 200° for two hours, they were almost completely isomerized to the corresponding cis-anhydrides (XI and XII).

This fact points to the considerably lower stability of the trans-anhydrides V and VI to heat, as compared with the corresponding trans-anhydrides having an angular methyl group, which give, by thermal isomerization, an equilibrium mixture of cis- and trans-isomers, the latter predominating [6].

The corresponding trans-acids (III and IV) behave in the same way when heated.

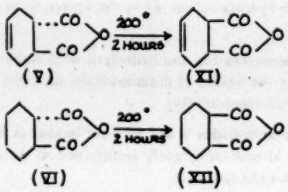
However, the acid chlorides prepared from the trans-monoesters VII and VIII are quite stable to heat. Thus the acid chloride XIII, obtained from the trans-monoester VII by the action of oxalyl chloride followed by distillation, is hydrolyzed quantitatively to the trans-acid III, and forms





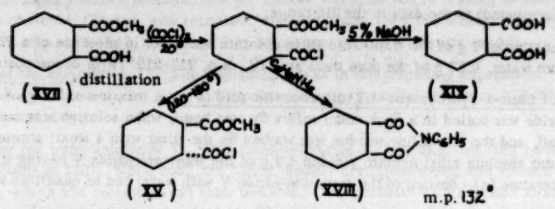
the normal trans-anilide (XIV) with aniline. Similarly, the acid chloride XV, obtained from the trans-monoester VIII, gives the pure trans-anilide XVI with aniline, and the pure trans-acid IV when hydrolyzed.

The acid chlorides of the monoesters of the cis series behave quite differently. Treatment of the cis-monoester XVII with oxalyl chloride followed by vacuum distillation of the product (bath temperature 120-130°) yielded a mixture of cis and trans acid chlorides, from which, after hydrolysis, the pure trans-acid IV was isolated in a yield of about 50% by means of crystallization. Treatment of this mixture of acid chlorides with aniline gave a crystalline product, from which the pure trans-anilide XVI, m.p. 126°, was isolated by means of crystallization. In addition to this anilide, another crystalline product, m.p. 100-102°, was isolated, and this was found to be a eutectic mixture of the trans-anilide XVI and the cis-phenylimide XVIII, and it gave no melting point depression with an artificially prepared mixture of these.

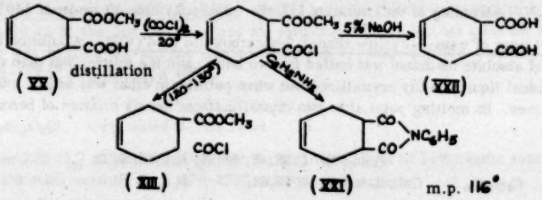


In a similar way, the distilled acid chloride obtained from the pure cis-monoester XX hydrolyzed to a mixture of cis- and trans-4-cyclohexene-1,2-dicarboxylic acids (not resolvable by crystallization), and treatment with aniline yielded the pure trans-anilide XIV, m.p. 136°. Apart from this anilide, fractional crystallization yielded another crystalline substance, m.p. 96-98°, and this was found to be identical with the eutectic mixture obtained from the trans-anilide XIV and the cis-phenylimide XXI.

This isomerization of the cis-acid chlorides takes place during their distillation, for these acid chlorides, when prepared from the pure cis-monoester XVII and XX and not distilled, give high yields of the cis-phenylimides when treated with aniline, and give the pure cis-acids XIX and XXII when hydrolyzed. This sort of



thermal isomerization of the cis form into the trans form in the preparation of acid chlorides has already been noted in a number of cases [8, 9], but it is almost absent in the case of cis-1-methyl-1,2-cyclohexanedicarboxylic and cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acids, which we have studied previously [10].



EXPERIMENTAL

Dimethyl ester of trans-4-cyclohexene-1,2-dicarboxylic acid (I). A mixture of 15 g of dimethyl fumarate [12], 70 ml of absolute benzene, and 30 g of 1,3-butadiene was heated in a steel tube at 200-205° for 3 hours 30 minutes. The benzene was distilled off, and the residue was distilled under reduced pressure. Redistillation yielded 19.5 g of the trans-diester I as a mobile colorless liquid, b.p. 137° (20 mm); n_D^{20} 1.4650; d_4^{20} 1.1234; found MR 48.96; calculated MR 49.02.

	Found %:	C 60.73; 60.45; H 7.27, 7.25
$C_{10}H_{14}O_4$.	Calculated %:	C 60.6; H 7.12

The dibromide: A chloroform solution of bromide was added in slight excess to a solution of 0.5 g of the trans-diester I in 10 ml of chloroform. The solvent was distilled off, and the crystalline product was crystallized twice from petroleum ether; m.p. 85-86°.

	Found %:	Br 44.73; 44.79
$C_{10}H_{14}O_4Br_2$.	Calculated %:	Br 44.64

Dimethyl ester of trans-1,2-cyclohexanedicarboxylic acid (II). The trans-diester I (10 g), dissolved in 70 ml of absolute methanol, was hydrogenated in presence of a Pd catalyst at room temperature, 1.18 liter of hydrogen (one molecule) being absorbed. The methanol was distilled off, and the residue, when vacuum-distilled, yielded 9.6 g of the trans-diester II, b.p. 135° (17 mm); n_D^{20} 1.4524; d_4^{20} 1.0945; MR found 49.39; MR calculated 49.49.

	Found %:	C 59.94; 59.92; H 7.99; 8.08
$C_{14}H_{16}O_4$.	Calculated %:	C 60.0; H 8.05

trans-4-Cyclohexene-1,2-dicarboxylic acid (III). A mixture of 10 g of the trans-diester I and 35 ml of a 20% solution of caustic potash was boiled for two hours, when solution was complete. The solution was mixed with charcoal and filtered. Acidification with hydrochloric acid yielded 7.9 g of the trans-acid III, m.p. 169-170°. After crystallization from 20% aqueous acetone the trans-acid melted at 171-172°, as given in the literature [3].

trans-1,2-Cyclohexanedicarboxylic acid (IV). a) A mixture of 5 g of the trans-diester II and 20 ml of a 20% solution of caustic potash was boiled for two hours, when solution was complete. Acidification of the solution yielded 4.1 g of the trans-acid IV, m.p. 214-216°. After crystallization from 20% acetone it melted at 218-220° (with decomposition), which corresponds to the data in the literature.

b) Hydrogenation of 1 g of the trans-acid III in absolute methanol in presence of a Pd catalyst yielded, after crystallization from water, 0.67 g of the pure trans acid IV, m.p. 217-219° (with decomposition).

Anhydride of trans-4-cyclohexene-1,2-dicarboxylic acid (V). A mixture of 7.5 g of the trans-acid III and 80 ml of acetyl chloride was boiled in a flask under reflux for two hours, when solution was complete. The acetyl chloride was distilled off, and the crystalline residue was washed on the filter with a small amount of petroleum ether. Two crystallizations from absolute ethyl acetate yielded 4.8 g of the trans-anhydride V having a constant m.p. of 188-189°, as given in the literature [4]. Boiling of the trans-anhydride V with water led to quantitative recovery of the trans-acid III.

Anhydride of trans-1,2-cyclohexanedicarboxylic acid (VI). The trans-anhydride V (0.8 g), dissolved in 30 ml of chloroform, was hydrogenated in presence of a Pd catalyst, 180 ml of hydrogen (one molecule) being absorbed. The solvent was distilled off, and the crystalline product was washed on the filter with a mixture of benzene and absolute ether (4:1). After crystallization from a mixture of benzene and ether, the trans-anhydride obtained (VI, 0.45 g) melted at 145-146°. The same trans-anhydride (VI) was readily obtained by the action of acetyl chloride on the trans-acid IV. According to the literature [2], the trans-anhydride VI melts at 140°.

Monomethyl ester of trans-4-cyclohexene-1,2-dicarboxylic acid (VII). A solution of 3 g of the trans-anhydride V in 30 ml of absolute methanol was boiled for two hours, and the solvent was then distilled off under reduced pressure. The residual liquid readily crystallized out when petroleum ether was added, and 2.8 g of the trans-monoester VII was obtained. Its melting point after two crystallizations from a mixture of benzene and petroleum ether (1:4) was 58-59°.

	Found %:	C 58.45; 58.39; H 6.54; 6.33
$C_9H_{12}O_4$.	Calculated %:	C 58.68; H 6.57

Monomethyl ester of trans-1,2-cyclohexanedicarboxylic acid (VIII). The trans-monoester VII (0.5 g), dissolved in 10 ml of benzene, was hydrogenated over a Pd catalyst. When one molecule of hydrogen had been absorbed, the solvent was distilled off. Treatment of the liquid residue with petroleum ether yielded a crystalline product (0.44 g) of m.p. 93-94.5° (the trans-monoester VIII), which melted, after recrystallization from a mixture of benzene and petroleum ether (1:5), at 95-96°, as given in the literature [7]. The same trans-monoester (m.p. 94-95°) was obtained when the trans-anhydride VI was boiled in absolute methanol.

Monomethyl ester of cis-4-cyclohexene-1,2-dicarboxylic acid (XX). A solution of 40 g of the anhydride of cis-4-cyclohexene-1,2-dicarboxylic acid [1] in 350 ml of absolute methanol was boiled for three hours. Methanol was distilled off under reduced pressure, and the liquid residue rapidly crystallized out on addition of petroleum ether, yielding 42.7 g of the cis-monoester XX, m.p. 74-76°. After two crystallizations from a mixture of absolute ether and petroleum ether (1:2), the cis-monoester had a constant melting point of 84-85°.

	Found %:	C 58.28; 58.30; H 6.50; 6.49
$C_9H_{12}O_4$.	Calculated %:	C 58.68; H 6.56

Hydrogenation of the cis-monoester XX in methanol in presence of a Pd catalyst yielded the saturated cis-monoester XVII, m.p. 68-69°, identical with the substance described in the literature [11].

Dimethyl ester of cis-4-cyclohexene-1,2-dicarboxylic acid (IX). A suspension of 5 g of cis-4-cyclohexene-1,2-dicarboxylic acid [1] in 50 ml of ether was treated with an ethereal solution of diazomethane. After removal of solvent, the residue was distilled, and yielded 4.9 g of the cis-diester IX, b.p. 114-115° (5 mm); n_D^{18} 1.4728.

	Found %:	C 60.42; 60.54; H 7.05; 7.34
$C_{10}H_{14}O_4$.	Calculated %:	C 60.6 H 7.12

Dimethyl ester of cis-1,2-cyclohexanedicarboxylic acid (X). Similar treatment of cis-1,2-cyclohexanedicarboxylic acid with diazomethane yielded the cis-diester X, b.p. 110-111° (5 mm); n_D^{18} 1.4590.

	Found %:	C 59.72; 59.72; H 7.91; 7.87
$C_{10}H_{16}O_4$.	Calculated %:	C 60.0; H 8.05

The same ester was prepared also by hydrogenation of the cis-diester IX in methanol in presence of a Pd catalyst.

Isomerization of the cis-diester IX. A solution of sodium methoxide was prepared from 7.5 g of sodium and 180 ml of absolute methanol, 2.8 g of the cis-diester IX was added, and the mixture was boiled for 15 hours. Methanol was distilled off under reduced pressure, and the residue was dissolved in a small amount of water. The solution was treated with charcoal, filtered, and acidified, whenit yielded 1.6 g (66.5%) ot trans-4-cyclohexene-1,2-dicarboxylic acid (III), m.p. 170-171°, undepressed by admixture with an authentic sample.

Isomerization of the cis-diester X. The procedure was as in the preceding experiment: from 3 g of the diester X a 75% yield was obtained of pure trans-1,2-cyclohexanedicarboxylic acid, m.p. 218-220° and identical with the sample prepared previously.

Isomerization of the trans-anhydride V. The trans-anhydride V (1 g; m.p. 186-188°) was heated in a flask under reflux for two hours at 200°. When cool, the liquid product crystallized out, and yielded 0.9 g of a yellow crystalline substance, which was recrystallized from benzene. The product (0.8 g) melted at 102-103°, undepressed by admixture with a pure sample of the cis-anhydride XI.

Isomerization of the trans-anhydride VI. The trans-anhydride VI (1 g; m.p. 144-145°) was heated for two hours at 200-205°. Hydrolysis of the colored liquid product was effected by boiling it with 4 ml of water until solution was complete, and the solution, when cool, yielded 0.75 g of pure cis-1,2-cyclohexanedicarboxylic acid (XIX), m.p. 189-190°, undepressed by admixture with an authentic sample.

Acid chloride of the trans-monoester VII (XIII). Oxalyl chloride (2 ml) was added to a solution of 2 g of the trans-monoester VII in 20 ml of absolute benzene, and the resulting solution was set aside for three hours at room temperature. Benzene was distilled off, and the liquid residue was vacuum-distilled, yielding 1.9 g of the acid chloride XIII, b.p. 112-112.5° (6 mm); n_D^{28} 1.4870.

Found %: Cl 17.85; 17.95

$C_9H_{11}O_3Cl$. Calculated %: Cl 17.51

The acid chloride XIII (0.7 g) was hydrolyzed at the boil with 10 ml of 10% caustic soda (10 minutes). On acidification 0.6 g of the trans-acid III, m.p. 170-172°, separated.

The trans-anilide XIV. A solution of 1 g of aniline in 10 ml of absolute ether was added slowly to a cooled (to 0°) solution of 1 g of the acid chloride XIII in 30 ml of absolute ether. The mixture was allowed to stand for one hour at room temperature and then treated with water. The ether layer was separated, washed successively with 5% hydrochloric acid, 5% caustic soda solution, and water, and finally dried over sodium sulfate. The ether was distilled off, and the crystalline residue was washed on the filter with a mixture of ether and petroleum ether (1:1). The product was 1.1 g of the trans-anilide XIV, m.p. 134-136°. After crystallization from 70% aqueous methanol it melted at 136-137°.

Found %: C 69.62; 69.41; H 6.53; 6.55; N 5.78; 5.64

$C_{15}H_{17}O_3N$. Calculated %: C 69.48; H 6.68; N 5.40

Acid chloride of the trans-monoester VIII (XV). By the procedure used for the acid chloride XIII, 2 g of the trans-monoester VIII yielded, after distillation, 1.8 g of the acid chloride XV, b.p. 114.5-115° (7 mm); n_D^{29} 1.4750.

Found %: Cl 17.49; 17.64

$C_9H_{13}O_3Cl$. Calculated %: Cl 17.33

On hydrolysis with 10% caustic soda solution, 0.7 g of the acid chloride XV yielded 0.65 g of trans-1,2-cyclohexanedicarboxylic acid (IV), m.p. 218-220°.

The trans-anilide XVI. By the usual procedure, 1 g of the acid chloride XV in ether solution yielded 1.15 g of the anilide, m.p. 123-124°. After recrystallization from 60% methanol the trans-anilide XVI had a constant m.p. of 126-127.5°.

Found %: C 69.25; 69.21; H 7.27; 7.24; N 5.47; 5.50

$C_{15}H_{19}O_3N$. Calculated %: C 68.96; H 7.33; N 5.36

The cis-phenylimide XVIII. Oxalyl chloride (1 ml) was added to a solution of 1 g of the cis-monoester XVII in 10 ml of absolute benzene, and the resulting solution was set aside for two hours at room temperature. Solvent was removed under reduced pressure (at 35-40°), and the residue was dissolved in 30 ml of absolute ether. The solution was cooled to 0° and stirred while a solution of 1 g of aniline in 10 ml of absolute ether was added slowly. The reaction product was allowed to stand for one hour at 0° and then treated as in the preceding experiment. The ether was driven off, and the crystalline product was washed on the filter with a mixture of ether and petroleum ether (1:1),

yielding 0.85 g of a substance of m.p. 120-126°. After recrystallization from 50% methanol, the cis-phenylimide XVIII melted at 132-133°.

Found %: C 73.53; 73.51; H 6.70; 6.83

$C_{14}H_{15}O_2N$. Calculated %: C 73.3; H 6.6

The cis-phenylimide XXI. By the procedure of the preceding experiment, 1 g of the cis-monoester XX was converted into the acid chloride, which, without being distilled, was caused to react with aniline, and yielded 0.75 g of the cis-phenylimide XXI, m.p. 115-116° (from 70% methanol).

Found %: N 6.31; 6.34

$C_{14}H_{13}O_2N$. Calculated %: N 6.16

Reactions of the acid chloride of the cis-monoester XVII. a) Oxalyl chloride (5 ml) was added to a solution of 5 g of the cis-monoester XVII in 50 ml of absolute benzene, and the resulting solution was set aside for two hours at room temperature. After removal of solvent under reduced pressure (30-35°), a liquid acid chloride remained.

Part of this acid chloride (0.5 g), without being distilled, was hydrolyzed at the boil with 7 ml of 5% caustic soda for five minutes. Acidification of the solution yielded 0.4 g of the cis-acid XIX, m.p. 191-192°, undepressed by admixture with an authentic sample (190-191°).

b) The remaining liquid acid chloride was vacuum-distilled, and yielded 4 g of a substance of b.p. 113-114° (5 mm) and n_D^{20} 1.4740. A portion (2 g) of the distilled acid chloride was hydrolyzed at the boil with 30 ml of 5% caustic soda for 10 minutes. Acidification yielded 1.8 g of an acid, m.p. 195-205°. This substance was recrystallized from water containing a little acetone, and 1.5 g of crystals of m.p. 200-212° was obtained. Recrystallization from 30% acetone yielded 0.8 g of the trans-acid IV, m.p. 218-220°, undepressed by admixture with an authentic sample. Fractional crystallization from water, applied to the mother liquors from the separation of the trans-acid IV, yielded 0.4 g of the cis-acid XIX, m.p. 189-191°.

c) The anilide was prepared by the usual method from 1 g of the distilled acid chloride. After removal of ether, 0.95 g of a crystalline substance of m.p. 95-110° was obtained. This substance was treated with warm ether, and the insoluble residue (0.5 g) melted, after crystallization from 60% methanol, at 126-127°, and gave no depression in admixture with the pure trans-anilide XIV. A heterogeneous crystalline product was obtained from the ether solution, and from this, by fractional crystallization, first from ether and then from 50% methanol, 0.2 g of another crystalline substance was isolated in the form of long fine needles, m.p. 100-102°. The analysis of this substance corresponded to an equimolecular mixture of the trans-anilide XIV and the cis-phenylimide XVIII. An artificially prepared mixture of XIV and XVIII melted, after crystallization from 50% methanol, at 100-102°, and showed no melting point depression in admixture with our second crystalline product of m.p. 100-102°.

Reactions of the acid chloride of the cis-monoester XX. a) The cis-monoester XX (5 g) was converted by the usual method into its acid chloride, and 0.5 g of this acid chloride, without being distilled, was hydrolyzed with 5% caustic soda. The product was 0.35 g of the cis-acid XXII, m.p. 166-167°, undepressed by admixture with a known sample.

b) Vacuum distillation of the remaining acid chloride yielded 3.8 g of acid chloride of b.p. 118-119° (7 mm) and n_D^{20} 1.4865. A portion (2 g) of this acid chloride was hydrolyzed in the usual way with 5% caustic soda, and 1.7 g of a mixture of acids was isolated. The mixture had a wide melting range (150-160°), and attempts to separate it by crystallization were not successful.

c) From 0.5 g of the distilled acid chloride, by treatment with aniline (0.5 g) in the usual way, 0.4 g of a crystalline substance of m.p. 95-120° was obtained. The residue (0.22 g) remaining after treatment with boiling ether melted at 132-135°, and this, when crystallized from 60% methanol, yielded 0.15 g of the pure trans-anilide XIV, m.p. 135-136°. The residue from the evaporation of the ether solution was crystallized from ether and from 50% methanol, and 0.1 g of a substance of m.p. 96-98° was isolated. This second crystalline product was found to be identical with an artificial mixture of equal amounts of the trans-anilide XIV and the cis-phenylimide XXI.

SUMMARY

1. 1,3-Butadiene has been condensed with methyl fumarate to give the dimethyl ester of trans-4-cyclohexene-1,2-dicarboxylic acid (I) in excellent yield. A number of derivatives of cis- and trans-4-cyclohexene-1,2-dicarboxylic acids have been prepared.

2. By the action of sodium methoxide, the isomerization of the cis-esters IX and X has been effected, the corresponding acids of the trans series (III and V) being obtained in good yield. It has been shown that at 200° the

trans-anhydrides V and VI are quantitatively isomerized to the corresponding cis-anhydrides (XI and XII).

3. Investigation has shown beyond doubt that the acid chlorides prepared from the cis-monoesters XVII and XX undergo thermal isomerization into the corresponding trans-acid chlorides, a process that occurs during distillation.

Received May 18, 1953

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HYDROGENATION AND DEHYDROGENATION OF HYDROCARBONS IN PRESENCE OF RUTHENIUM AND RHODIUM CATALYSTS OF LOW METAL CONTENT

Kh. M. Minachev, N. I. Shuikin, and I. D. Rozhdestvenskaya

Ruthenium and rhodium catalysts have received very little application in hydrogenation and dehydrogenatio. catalysis. This fact is to be explained first by the extreme rarity of these metals in nature, and second by their almost complete insolubility, not only in the usual acids, but also in aqua regia. The preparation of their salts and oxides is, therefore, associated with considerable difficulties. Apart from this, there are indications in the literature that ruthenium supported by asbestos or active charcoal has a vigorous decomposing effect on cyclohexane, without effecting any appreciable dehydrogenation. Thus, Zelinsky and Turova-Polyak [1] in experiments on the dehydrogenation of cyclohexane in presence of a 30% ruthenium catalyst (on asbestos) found that this catalyst begins to dehydrogenate cyclohexane already at 250°, but the benzene formed, even under these mild conditions, was broken down to methane. Similar results were obtained by Borisov and Stepanov [2] in the dehydrogenation of cyclohexane in presence of a 30% ruthenium catalyst (on active charcoal). Rhodium catalysts, judging from the results of the same exploratory investigations, do not have any great tendency to induce scission, but their dehydrogenating propensity has received insufficient study. In the investigations cited it is shown that ruthenium and rhodium catalysts are very efficient for the hydrogenation of the benzene ring.

Fischer, Bahr, and Meusel [3] have used metallic ruthenium and finely dispersed ruthenium on asbestos (metal content 35%) in the catalytic reduction of carbon dioxide to methane and higher hydrocarbons (at 125-150°). The authors state that the catalysts become more active when given a preliminary treatment for two hours with air at 300-400°, with 5% nitric acid, or with potassium or rubidium carbonate.

Kiperman [4] showed that the activation energy for the decomposition of ammonia at a Ru/silica gel catalyst is 59,950 cal/mole, whereas for the same reaction at vanadium and osmium catalysts he found 45,000 cal/mole. The author ascribes this difference to the high hydrogen adsorption at a ruthenium surface.

Dunworth and Nord [5] have recently used 5% rhodium on active charcoal in the reduction of aromatic and aliphatic nitro compounds, and also for the hydrogenation of carbon-carbon double bonds in various fatty acids. The authors showed that a nitro group in a benzene ring is reduced much more rapidly than the nitro group of an aliphatic compound. The carbon-carbon double bond in fatty acids is hydrogenated smoothly, but considerably more slowly with this catalyst than with colloidal rhodium supported on polyvinyl alcohol [6].

In our previous communications [7] we have described the hydrogenation and dehydrogenation properties of platinum, palladium, nickel, and cobalt catalysts in their relation to the ratio of metal to carrier. It was shown that these catalysts could be successfully used for the hydrogenation and dehydrogenation of hydrocarbons. In the same investigations the structural peculiarities of platinum and palladium catalysts were characterized by X-ray analysis. It was shown that platinum retains its crystal structure on an amorphous carrie r right down to the minimum concentration of 0.03%. On the basis of these results we made a suggestion concerning the way in which the metal is distributed on the surface of charcoal, and this was later confirmed by direct determinations.

Investigation of the structure of palladium catalysts showed that finely dispersed palladium on charcoal preserves its crystal structure right down to a metal concentration of 0.05%. It was shown by a study of the X-ray structures of Pt and Pd catalysts that had received prolonged exposure to the conditions of hydrogenation and dehydrogenation reactions that no recrystallization occurred under these conditions.

In continuation of our investigation of the specific characteristics of catalysts of low metal content, we have studied the hydrogenation and dehydrogenation properties of finely dispersed ruthenium and rhodium, supported on various carriers. Our interest was directed particularly to the following points: 1) the variation of the dehydrogenation activities of the catalysts with temperature; 2) the ability of these catalysts to bring about hydrogenation of the benzene ring, of cycloalkenes, and of alkenes; 3) the values of the activation energies for the dehydrogenation of cyclohexane over these catalysts; and 4) the elucidation of the structural peculiarities of these catalysts.

EXPERIMENTAL

Preparation of catalysts. Four catalysts were prepared: 1) 1% Ru on aluminum oxide; 2) 1% Ru on active charcoal; 3) 1% Rh on aluminum oxide; and 4) 1% Rh on active charcoal. The rhodium catalysts were prepared by impregnation of the corresponding carriers with a solution of H_3RhCl_6 at room temperature, and the ruthenium catalysts were prepared under the same conditions from a solution of NH_4RuCl_5NO.

Procedure. The catalysts, after being dried at 120°, were reduced with electrolytic hydrogen directly in the reaction tube at 325-330°. The experiments on the hydrogenation and dehydrogenation of hydrocarbons were carried out in the usual continuous-flow apparatus, as described previously [7]. In all cases, the volume of reduced catalyst was 50 ml. The conversion of cyclohexane into benzene, and of benzene into cyclohexane, was followed refractometrically [8]. The gas analysis was carried out in the usual VTI gas analyzer.

Experimental Results

The extent to which cyclohexane is dehydrogenated over these catalysts is shown for various temperatures in Table 1 (the space velocity for the passage of cyclohexane was 0.3 liter per liter of catalyst per hour). As will be seen from Table 1, rhodium catalysts already have very high activity at 300°, and at 340-360° the conversion of cyclohexane into benzene attains 92-95%. Ruthenium catalysts were found to be less active, even at elevated temperatures. The higher activity of the catalysts, both ruthenium and rhodium, on aluminum oxide is due to the fact that in the samples taken for investigation the metal content was three times as high as in the corresponding catalysts on charcoal. The essential difference between the catalysts studied by us and those studied in previous investigations [1, 2] is that they did not bring about scission of the cyclohexane ring below 300°. When cyclohexane was passed over these catalysts at 320-380°, the issuing gas contained 3.4-25.6% of methane hydrocarbons. This behavior in our catalysts is probably to be explained by the low metal content (as % of amount of carrier) and the considerable space velocity of the cyclohexane.

TABLE 1

Extent of Dehydrogenation of Cyclohexane over Rhodium and Ruthenium Catalysts at Various Temperatures

Catalyst	Temperature of experiment (°C)					Amount of metal in catalyst taken (g)
	300	320	340	360	380	
	Conversion of cyclohexane (%)					
Rh-charcoal	56	72	83	92	–	0.11
$Rh-Al_2O_3$	76	84	95	–	–	0.30
Ru-charcoal	20.8	28.5	37.4	46.5	55	0.12
$Ru-Al_2O_3$	28.5	34.8	43.6	52.8	67.4	0.30

Hydrogenation Properties of Rhodium and Ruthenium Catalysts

All four catalysts were very active in the hydrogenation of the benzene ring, and also of alkenes and cycloalkenes. The dependence of the degree of conversion of benzene on the space velocity is shown for rhodium-charcoal and ruthenium-charcoal catalysts in Fig. 1. As will be seen from this figure, the rhodium catalysts completely hydrogenated benzene at a space velocity of 0.13 liter per liter of catalyst per hour. With further increase in the

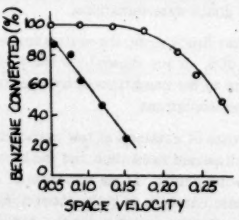

Fig. 1. Dependence of the degree of conversion of benzene on the space velocity at 150°: o = 1% Rh-charcoal; • = 1% Ru-charcoal.

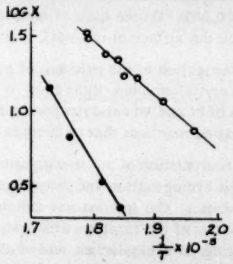

Fig. 2. Variation of the rate of dehydrogenation of cyclohexane with the temperature in presence of the catalyst: o = 1% Rh-charcoal; • = 1% Ru-charcoal.

rate of passage of benzene, the percent conversion gradually falls, and at a space velocity of 0.28 it is 49. Under the same conditions the ruthenium catalyst promotes the hydrogenation of benzene in appreciably lower degree, but over the space velocity range of 0.05-0.07 liter of benzene per liter of catalyst per hour, the degree of conversion ranges correspondingly from 90 to 60%.

The results obtained for the hydrogenation of 1-methylcyclopentene and 1-octene are given in Table 2. These experiments were carried out at 140-143° at a space velocity of 0.11-0.12 liter per liter of catalyst per hour. The synthesis and properties of the hydrocarbons taken for hydrogenation have been described by us in a previous paper [7]. The results in Table 2 show that the properties of the hydrocarbons obtained are in close accord with those given in the literature [9, 10].

TABLE 2

Hydrogenation of Unsaturated Hydrocarbons over Rh-Charcoal and Ru-Charcoal Catalysts

Catalyst	Substance hydrogenated					
	1-methylcyclopentene			1-octene		
	Properties of Catalyzates					
	B.p. (°C)	n_D^{20}	d_4^{20}	B.p. (°C)	n_D^{20}	d_4^{20}
Rh-charcoal	71.4-72.2 (756 mm)	1.4102	0.7474	125.4-126 (758 mm)	1.3976	0.7072
Ru-charcoal	71.6-82.0 (757 mm)	1.4100	0.7471	125.4-126 (756 mm)	1.3972	0.7073

Kinetics of the Dehydrogenation of Cyclohexane over Rh-Charcoal and Ru-Charcoal Catalysts

No data exist in the literature on the kinetics of the dehydrogenation of cyclohexane over ruthenium and rhodium catalysts. We decided to determine the activation energies for these reactions and to compare the results with those for platinum and palladium catalysts. The experimental conditions were similar to those described in a previous paper [11]. The results are given in Table 3. Fig. 2 shows the variation of the rate of reaction with temperature, and it will be seen that the points give close fit to straight lines. This indicates that the variation in the rate of the dehydrogenation of cyclohexane with temperature obeys the Arrhenius law. The values of Q and K_0 found for the rhodium catalyst are fairly close to those for a palladium catalyst [12] ($Q = 15{,}800$ and $K_0 = 5{,}754 \cdot 10^5$) and are practically identical with those for platinum catalyst [11] ($Q = 15{,}250$ and $K_0 = 1.66 \cdot 10^5$). The values obtained for the ruthenium catalyst differ greatly from the values given by metal catalysts and approach the values obtained for the dehydrogenation of cyclohexane over chromium oxide [13].

This considerable difference between the activation energy for the dehydrogenation of cyclohexane over a ruthenium catalyst and that for the same reaction over other metal catalysts may be a result of a difference in crystal lattice. Ruthenium has a hexagonal lattice having the parameters $a = 2.695$ A and $c = 5.273$ A, whereas Pt,

TABLE 3

Kinetic Results on the Dehydrogenation of Cyclohexane in Presence of Ruthenium-Charcoal and Rhodium-Charcoal Catalysts

Catalyst	Expt. No.	Temp. (°C)	v_0 (in 10 min.)	Conversion (x, %)	log x	$\frac{1}{T} \cdot 10^{-3}$	Activation energy α, and pre-exponential term K_0
Rh-charcoal	1	285	372	33.7	1.5276	1.792	
	2	276	270.6	24.5	1.3892	1.821	
	3	260	193.6	17.5	1.2430	1.876	
	4	248	131.0	11.9	1.0755	1.919	Q = 16,800
	5	236	84.4	7.6	0.8806	1.965	$K_0 = 1.44 \cdot 10^9$
	6	260	189.0	17.1	1.2330	1.876	
	7	270	250.6	22.8	1.3579	1.842	
	8	285	341.6	31.0	1.4914	1.792	
Ru-charcoal	1	277	42.0	3.5	0.5441	1.818	
	2	269	29.0	2.4	0.3802	1.845	Q = 30,200
	3	294	80.2	6.8	0.8325	1.764	$K_0 = 1.77 \cdot 10^{18}$
	4	305	173	14.4	1.1584	1.730	

Pd, and Rh have cubic lattices. Also, according to data in the literature [14], ruthenium can sorb about 1520 volumes of hydrogen per unit volume of metal. Hence, the high activation energy for the dehydrogenation of cyclohexane over a ruthenium catalyst may be due to the high concentration of hydrogen at the surface of this catalyst.

X-ray Investigation of the Catalysts*

The catalyst samples were examined with chromium radiation of the K series (λ = 2.285 A); exposure 12 hours at 10 milliamp and 30 kv.

Ruthenium catalysts. Catalyst No. 1 (1% Ru on charcoal) gave only one weak line, corresponding to d = 2.06 A; the discrepancy from the value given in tables (2.13 A) for the 110 line of Ru is probably to be explained by inaccuracy in the measurement of the line on the X-ray picture. Also, the possibility cannot be excluded that some deformation of the Ru lattice occurs under the influence of the carrier.

Catalyst No. 3 (1% Ru on Al_2O_3) gave a series of lines (d = 2.12, 1.91, and 1.37 A). The value of 2.12 corresponds to the 110 Ru lines, and d = 1.91 and 1.37 are characteristic lines of γ-Al_2O_3 (hkl = 004 and 044). In both cases the values were in agreement with those given in tables. The lattice parameters were calculated, with the following results:

Ru catalyst No. 1: a = 2.690 A

Ru catalyst No. 3: a = 2.697 A

The value given in reference tables is 2.697 A. Owing to the absence of other reflections, the parameter c was not determined. For γ-Al_2O_3 the value a = 7.90 A was obtained (tabular value 7.91 A).

Rhodium catalysts. Catalyst No. 2 (1% Rh on charcoal) gave only one weak line (Rh 111), very diffuse and difficult to measure (d = 2.04 A; the tables give 2.20 A). Catalyst No. 4 (1% Rh on Al_2O_3) gave a weak Rh 111 line, d = 2.14 A, and characteristic γ-Al_2O_3 lines (d = 1.92 and 1.38 A). For Rh catalyst No. 4 the value of a was found to be 3.74 A, and for Catalyst No. 2 the value 3.60 A was found (the tables give 3.79 A).

In Catalyst No. 4 γ-Al_2O_3 had a normal undeformed lattice. On all of the X-ray pictures the lines were very wide and diffuse, indicating a very high degree of dispersion (of the order of 10^{-7} cm) in the catalysts investigated.

SUMMARY

1. A study has been made of the hydrogenation and dehydrogenation propensities of rhodium and ruthenium catalysts supported on various carriers.

2. It has been shown that the activity of these catalysts for the hydrogenation of alkenes, cycloalkenes, and the benzene ring is close to that of a platinum catalyst.

3. The activation energies for the dehydrogenation of cyclohexane over ruthenium and rhodium catalysts have been determined.

Received April 1, 1953

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* The investigation of the X-ray structures of the catalysts was carried out by A. M. Rubinshtein, and we wish to express our thanks for this.

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INVESTIGATION BY THE ULTRACENTRIFUGE SEDIMENTATION METHOD OF THE MOLECULAR WEIGHT DISTRIBUTION FUNCTION OF POLYAMIDES

COMMUNICATION 1. DETERMINATION OF THE DISTRIBUTION FUNCTION OF POLYAMIDES FROM SEDIMENTATION CONSTANTS

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The study of the molecular weight distribution function of polymers presents a problem that has not yet been completely solved, in spite of its exceptionally high importance for the chemistry of macromolecular compounds. The extensively used laboratory method of fractional precipitation, followed by the construction of summative and differential molecular weight distribution curves from the fractionation data, contains errors that cannot be allowed for, since there always remains an unknown distribution function for each separate fraction. Theory and experiment show that, in the precipitation, the separating polymer fractions always carry with them a certain amount of substance belonging to all of the remaining fractions.

Recently, particularly in Svedberg's laboratory, the ultracentrifuge has been used in experiments on the determination of the distribution function of polymers. These investigations have shown the possibility, in principle, of solving our problem and have given us some idea of the molecular weight distribution of certain polymers (polystyrene, polymethyl methacrylate, and cellulose ethers and esters). The results of these investigations have been given in a review by Kinell and Ranby [1]. However, detailed examination of these results shows that the technique of the study of distribution functions and, in particular, the method used for the analysis of the experimental results cannot be regarded as completely satisfactory. In these experiments the polymer was fractionated by precipitation from solution, and each fraction was studied separately with the aid of the ultracentrifuge. The distribution function of each separate fraction was then treated arbitrarily as a triangle, the width of which was evaluated from the width of the experimental peak on the sedimentation diagram. Summation of the triangles corresponding to the separate fractions then led to the distribution function of the polymer with respect to sedimentation constants s, i.e., $\frac{dc}{ds} = f(s)$ (c is the concentration by weight, and s is the sedimentation constant). To pass from this function to the molecular weight distribution function characterizing the polymer $\frac{dc}{dM} = \varphi(M)$, it is necessary to make further, independent measurements (for example, of diffusion or of sedimentation equilibrium). With the exception of one old investigation (Signer and Gross) no such measurements have been carried out for any of the polymers.

We must here point out a fundamental experimental difficulty in working with linear polymers: measurements of sedimentation and diffusion must be made at limiting dilutions so that the dependence of these values on concentration, which arises from the interaction of the macromolecules in solution, does not obscure the essential picture and can be taken into account in the form of a small correction (extrapolation to infinite dilution). The present refractometric methods used in ultracentrifuge experiments set a limit to the sensitivity of concentration measurements. Hence, a convenient subject for the study of the distribution function is provided by a linear polymer for which the degree of polymerization is not too high and the concentrational variations not too great at concentrations of 0.5-0.1% by weight.

In the present investigation, we selected mixed polyamides having molecular weights of up to 60,000. In this case, which is a simple one from the experimental point of view, we have succeeded in working out a method for determining the molecular weight distribution function that is free from any arbitrary element and contains no *a priori* assumptions.

We have retained the method, introduced by the Swedish workers, of preliminary fractionation followed by investigation of separate fractions. This increases the resolving power of the method, since the distribution function for each fraction is found to be a simple one. Experiment shows that it can be approximated very closely by a Gauss function. As a result, the quantitative analysis of the experimental results is considerably simplified. Also, such a method does not introduce any arbitrary element, for the complete distribution function is determined separately for each fraction, and this is followed by the summation of the curves for all of the fractions. Finally, as will be shown

below, by combining sedimentation and diffusion results in a simple and natural way, we pass from sedimentation constant distribution function $\frac{dc}{ds}$ to the required molecular weight distribution function $\frac{dc}{dM}$.

The study of the molecular weight distribution function of polyamides is of interest not only because it enables us to obtain a deeper understanding of this new and little studied class of macromolecular compounds; it is of still greater importance as a method that enables us to understand and establish with exactness the reaction mechanism by which these substances are formed. The equation for the formation of a polyamide has the following form:

$$x\,H_2N(CH_2)_nNH_2 + x\,HOOC(CH_2)_mCOOH \rightleftharpoons H[HN(CH_2)_nNHCO(CH_2)_mCO]_xOH + (x-1)H_2O.$$

EXPERIMENTAL

Preparation of Samples for Investigation

Four samples of a mixed polyamide were investigated as solutions in methanol. The samples differed in degree of polycondensation. Sample No. 1 had a molecular weight of 30,000 (according to the viscosity of its methanol solution), and the molecular weights of Samples No. 2 and 3 were 20,000 and 46,000 respectively. Sample No. 4 was prepared by heating a mixture of equal amounts of two polyamide fractions, the first fraction having a molecular weight of 15,900, and the second a molecular weight of 58,000 (denoted by 1'' and 2'' respectively). In order that the mixing might be more complete, the two fractions were first dissolved in methanol and precipitated by pouring the resulting solution into ether. The mixture of fractions was dried in a current of nitrogen and then placed in a sealed tube, which was heated for six hours at 220°. The resulting polyamide had a molecular weight of 31,000 (according to the viscosity of its methanol solution).

Fractionation

Ether was gradually added to 1% solution of the polyamide in methanol until a slight stable turbidity appeared which became gradually more intense as stirring continued. After 2-3 hours, when the amount of precipitate formed had become constant, the fraction was filtered off, washed, and dried in a current of nitrogen under reduced pressure at room temperature. The last fraction was separated after evaporation of the solution to a concentration of 3-4%. In order to avoid losses, after each washing of the precipitate the filtrate was united with the main filtrate containing the residual portion of polyamide. The precipitate sticking to the funnel, walls of the flask, etc. was carefully washed off with hot alcohol; the solution was evaporated down, and the polyamide obtained was assigned to the losses. In Table 1 we give results of the fractionation of the four polymer samples.

TABLE 1

Fractionation of Polyamides

Polyamide Number	Fraction number	Weight of fraction (g)	Weight of losses (g)	Total weight of fraction (g)	Proportion of fraction (by weight)	Viscosimetric mol. wt. of fraction
1	1	0.75	0.20	0.95	0.153	47,500
	2	2.75	0.41	3.16	0.507	29,000
	3	0.75	0.13	0.88	0.141	29,000
	4	0.55	0.11	0.66	0.165	19,500
	5	0.60	0.0	0.60	0.094	6,500
2	1	1.58	0.02	1.60	0.280	26,000
	2	0.79	0.10	0.89	0.155	23,500
	3	0.70	0.12	0.82	0.140	23,500
	4	1.12	0.27	1.39	0.240	14,500
	5	1.05	0.07	1.12	0.185	6,800
3	1	2.86	0.03	2.87	0.162	–
	2	7.80	0.07	7.87	0.444	–
	3	5.38	0.08	5.46	0.310	–
	4	1.42	0.06	1.48	0.084	–
4	1	1.37	0.05	1.42	0.619	–
	2	0.72	0.04	0.76	0.330	–
	3	0.20	0.0	0.12	0.051	–

Experimental Results of Sedimentation Constants and Diffusion Coefficients

The sedimentation constants of the polyamide, dissolved in methanol, were measured in a Svedberg ultracentrifuge [2]. The experiments were carried out at a polyamide concentration of 0.5%. The investigated solution was placed in a Textolite cell fixed in the ultracentrifuge rotor. The measurements were carried out at a rotor speed of 60,000 rpm and at 20-25°. The temperature of the rotor could be measured accurate within 0.1°. For the recording of the sedimentation, Lamm's scale method [3] was used; this utilizes the difference in refractive index between solvent and solution and is based on the proportionality between the refractive index gradient and the concentration gradient. The experiments yield a series of curves, obtained at various times after the beginning of sedimentation, for the variation of the concentration gradient along the cell $\frac{dc}{dx} = f(x)$; from these we find the position of the maximum concentration gradient, i.e., the boundary between the solution and the solvent that has already been freed from dissolved polymer owing to its sedimentation. The $\frac{dc}{dx} = f(x)$ curves have definite widths, owing to the polydispersity of the fraction. The rate at which the maximum of the curve moves corresponds to the sedimentation rate for the "most probable" macromolecules of the given fraction.

From these results, we may calculated the sedimentation constant of the dissolved polymer: for this purpose we use the exact formula for the rate of movement (sedimentation) of a polymer in a centrifugal field:

$\frac{1}{\omega^2 x} v = \frac{1}{\omega^2 x} \frac{dx}{dt} = s$ (s is the sedimentation constant for the distribution maximum, which depends only on the molecular weight of the corresponding macromolecules; ω is the angular velocity of rotation; x is the coordinate, i.e., the distance from the center of the rotor). In this formula a certain degree of inhomogeneity in the centrifugal field is taken into consideration Integrating this equation, we obtain:

$$\ln x - \ln x_0 = s\omega^2 (t - t_0),$$

[x_0 is the initial position of the maximum (measured along the radius from the center of the rotor); x is the position at time t].

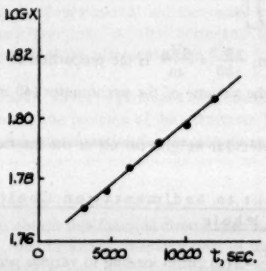

Fig. 1. Graph of log $x = f(t)$ for a polyamide fraction in methanol at a concentration of 0.5 g per 100 ml.

Hence, if we construct the graph for the change in ln x for the maximum of the curve against time, a straight line is obtained. Fig. 1 shows such a graph for a typical fraction. The slope of the curve divided by ω^2 gives the constant s for the distribution maximum. The value of s is adjusted to standard conditions (20°) by means of the correction factor $k = \frac{\eta_t}{\eta_{20}} \frac{1 - V_{20}\rho_{20}}{1 - V_t\rho_t}$. ($\eta_t$ and η_{20} are the viscosities of the medium at t° and 20°; V_t and V_{20}, ρ_t and ρ_{20} are the specific partial volumes of the polymer and the densities of the solution). Our experimental results are given in Table 2.

One of us has already given a detailed description of the apparatus used for the determination of diffusion coefficients [4]. It consists of a water thermostat in which the cell containing the solution to be investigated is placed, and an optical arrangement for recording the diffusion process by Lamm's method. The solution is formed as a layer under the solvent in a glass cell having a side tube, which, being at the middle of the cell, where the boundary is to be formed, permits the removal of the first portion of the solution, which may mix with the solvent by convection. This method enables the boundary between the layers to be made narrower and sharper. At definite intervals (six hours) after the establishment of the boundary, the scale is photographed through the solution. The duration of the experiment is 42-48 hours; the temperature of the thermostat is 25 ± 0.005°. From the experimental diffusion curves $\frac{dc}{dx} = f(x)$ obtained by examination of the photographs, the curve moments of zero (m_0), first (m_1), and second (m_2) orders are calculated, and hence the diffusion coefficients:

$$D = \left(\frac{m_2}{m_0} - \frac{m_1^2}{m_0^2}\right) \frac{G^2}{2t} \frac{T_{20}\eta_t}{T_t\eta_{20}} = \frac{\sigma^2}{2t},$$

(G is the factor for the photographic magnification of the scale; $\frac{T_{20}\eta_t}{T_t\eta_{20}}$ is the factor necessary for the adjustment of

the diffusion coefficients to normal conditions). From five or six curves relating to one experiment, the calculated values of σ^2 are plotted as a function of t, and the diffusion coefficients are calculated from the slopes of the resulting straight lines. This method of calculation avoids error due to the finite thickness of the boundary between the layers at zero time. The values of diffusion coefficients obtained are given in Table 2.

TABLE 2

Sedimentation Constants and Diffusion Coefficients for Polyamide Fractions

Polyamide number	Fraction number	Sedimentation constant $\cdot 10^{13}$	Diffusion coefficient $\cdot 10^{7}$	Polyamide number	Fraction number	Sedimentation constant $\cdot 10^{13}$	Diffusion coefficient $\cdot 10^{7}$
1	1	2.2370	3.8720	3	1 + 2	2.2750	3.3760
	2	2.1138	5.4470		1	2.5060	2.4310
	3	2.0780	5.7620		2	2.2040	3.4660
	4	1.8900	6.0770		3	2.0700	3.6000
	5	1.5450	13.2360		4	1.7340	7.7870
	1 + 2 + 3	2.1440	5.0000	4	1	1.9070	5.0870
2	1	1.9359	4.8620		2	1.7986	6.0777
	2	1.7790	5.9400		3	1.2930	10.8950
	2 + 3	1.8407	5.8200		1"	1.6470	7.5850
	3	1.9200	6.2750		2"	2.4070	3.0160
	4	1.7080	7.1130				
	5	0.9979	23.5000				

In order to calculate the molecular weight it is necessary to know the partial specific volume V of the polyamide in methanol. In order to find this quantity the densities of the pure solvent and of a 0.5% polyamide solution were measured. The calculation of the partial specific volume was made by the formula:

$$V = V_a \left[\frac{1}{m} - \frac{100}{p} \left(\frac{1}{m_0} - \frac{1}{m} \right) \right],$$

[m is the weight of solution in the pycnometer; m_0 is the weight of solvent; $\frac{p}{100} = \frac{gV_a}{m}$ is the proportion of the substance by weight; g is the concentration in g/ml (g = 0.005 g/ml); V_a is the volume of the pycnometer (40 ml)]. V_{20} was found to be 0.884.

Table 1 gives the results of determinations of the most probable molecular weights for all of the fractions studied.

Determination of the Distribution Function with respect to Sedimentation Constants for Each Fraction and for the Sample of Polymer as a Whole

The ultracentrifuge gives us, for each fraction, a series of curves $\frac{dc}{dx} = f(x)$ corresponding to various periods of time after the beginning of sedimentation. Examination of the curves $\frac{dc}{dx} = f(x)$ shows that they are somewhat unsymmetrical. For reasons that we shall consider below, in the course of sedimentation the boundary becomes diffuse, i.e., the curve $\frac{dc}{dx} = f(x)$ has a certain width. For this reason the region of the solution corresponding to the beginning of the curve is under a lower centrifugal force than that corresponding to the end of the curve.

Let us examine a point on the curve at Δx from the distribution maximum. The macromolecules corresponding to this coordinate move under a centrifugal acceleration of $\omega^2 x'$, which differs from the acceleration $\omega^2 x$ acting at the distribution maximum. The additional velocity Δv acquired under the action of this extra force will be related to the rate of movement of the peak as follows:

$$\frac{\Delta v}{v} = \frac{\omega^2 x' - \omega^2 x}{\omega^2 x} = \frac{\Delta x}{x}.$$

If we regard the broadening of the curve, i.e., Δx (Δx is the divergence from the central point of the curve), as a quantity that is to a first approximation proportional to the time, we obtain for the displacement due to the

inhomogeneity of the field:

$$\varphi = \tfrac{1}{2}\Delta vt = \tfrac{1}{2}vt\frac{\Delta x}{x} = \tfrac{1}{2}\Delta x\,\frac{x-x_0}{x},$$

(x is the coordinate of the center of the curve; $x-x_0$ is the displacement of the peak since the beginning of the experiment). The correction may be up to $\pm$ 4% of the divergence from the middle point of the curve (Δx). In introducing this correction to the width of the curve, we must, of course, make also corresponding alterations in the ordinates of all points of the curve, so that the area under the curve shall remain unchanged:

$$\frac{dc}{dx} = \left(\frac{dc}{dx}\right)' \left(1 + \frac{x-x_0}{2x}\right).$$

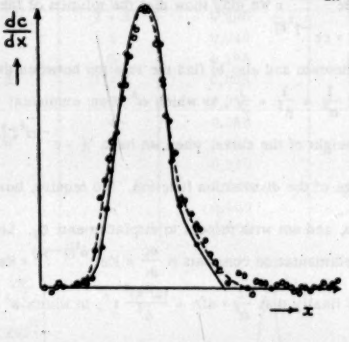

Fig. 2. Experimental sedimentation curve: -o- before correction; -o- after correction for the inhomogeneity of the ultracentrifuge field.

All curves are thus reduced to the form that they would have had if the field of force had been uniform. Fig. 2 shows the experimental curve before and after correction. The correction, although not great, renders the curve symmetrical with respect to the distribution maximum. In such a form the experimental curves can be taken as the basis for the calculations.

Let us examine the physical causes of the broadening of the sedimentation peak with time. They may evidently be of two kinds: first, the polydispersity of the given fraction, and second, diffusion of molecules close to the sedimentation boundary. For polyamides, with their comparatively low molecular weights and corresponding considerable diffusion coefficients, the diffusion broadening will be a quantity of the same order as the broadening due to polydispersity. For this reason a detailed analysis of the phenomenon is required here.

Using Fig. 2, let us examine the movement of macromolecules close to the sedimentation boundary with respect to the movement of the distribution maximum, for which we already (above) calculated the sedimentation constant. Let us denote the displacement of a macromolecule with respect to the position of the maximum by ξ. Our experimental curve (corrected) can evidently be transformed into a distribution function for macromolecules with respect to displacements simply by transfer of the origin; it will thus be:

$$\frac{dc}{d\xi} = f(\xi).$$

We obtain this function from experiment. The displacement ξ is made up of two statistically independent quantities: ξ_1, the diffusional displacement of the macromolecules, and ξ_2, the displacement due to the statistical scatter of molecular sizes within the fraction studied:

$$\xi = \xi_1 + \xi_2.$$

The distribution function with respect to displacements ξ_1 is known from the diffusion laws:

$$\frac{dc}{d\xi_1} = \varphi_1(\xi_1) = \frac{c_0}{\sqrt{4\pi Dt}}\, e^{-\frac{\xi_1^2}{4Dt}}.$$

There is also, of course, a certain scatter of the diffusion constant D within each fraction, but this gives only a correction of the second order in the distribution function. The distribution function with respect to the displacements ξ_2, i.e., $\frac{dc}{d\xi} = \varphi_2(\xi_2)$, is the required distribution function for the polydisperse substance with respect to sedimentation constants. Since the displacements ξ_1 and ξ_2 are statistically independent, in accordance with statistical laws we obtain:

$$\frac{dc}{d\xi} = f(\xi) = \int_{-\infty}^{\infty} \varphi_1(x)\varphi_2(\xi - x)dx = \int_{-\infty}^{\infty} Be^{-\frac{x^2}{4Dt}} \varphi_2(\xi - x)dx.$$

Hence, the function sought, $\varphi_2(\xi)$, is found as the solution of an integral equation of the Feldholm type, the left hand side of which is the function $\underline{f}(\xi)$, which we know in graphical form (the experimental curve). This equation may be solved by various methods, according to the form of the function $\underline{f}$, but it is particularly simple to solve when the empirical function $\underline{f}(\xi)$ can be closely approximated by a Gauss function, which is indeed so in our case. A Gauss curve is shown in Fig. 3, and the empirical points for the fraction that we used to demonstrate the method of calculation are indicated on this curve. It will be quite obvious that the experimental results fit the Gauss curve very well. The same applies to a large number of experimental curves that we have obtained. As will be shown later, this fact is a consequence of the fact that within every fraction the molecular weight distribution function is Gaussian.

If we write $\underline{f}(\xi) = Ae^{-\alpha^2\xi^2}$, and also $\varphi_1(\xi) = Be^{-\beta^2\xi^2} = Be^{-\frac{\xi^2}{4Dt}}$, we may show that the solution of the integral equation is also a Gauss function, i.e., the required $\varphi_2(\xi_2) = ce^{-\gamma^2\xi_2^2}$.

Simple algebraic manipulation enables us to prove this theorem and also to find the relation between the constants characterizing the distribution range. It is found that $\frac{1}{\alpha^2} = \frac{1}{\beta^2} + \frac{1}{\gamma^2}$, in which α^2 is an empirical quantity that may be found from the value of ξ at half of the height of the curve, when we have $\frac{1}{2} = e^{-\alpha^2\xi_{1/2}^2}$, and $\alpha^2 = \frac{\ln 2}{\xi_{1/2}^2}$; β^2 is $\frac{1}{4Dt}$; and γ^2 characterizes the required range of the distribution function. We require, however, the distribution function with respect to sedimentation constants, and not with respect to displacements ξ_2. Let us suppose that the required distribution function with respect to sedimentation constants is $\frac{dc}{ds} = Ke^{-\delta^2(s-s_0)} = Ke^{-\delta^2\Delta s^2}$; applying equation $\xi_2 = (s-s_0)\omega^2 x t$, we find that $\gamma^2 = \frac{\delta^2}{(\omega^2 x)^2 t^2}$, and finally that $\frac{1}{\alpha^2} = 4Dt + \frac{(\omega^2 x)^2}{\delta^2} t^2$, in which δ^2 is the required quantity.

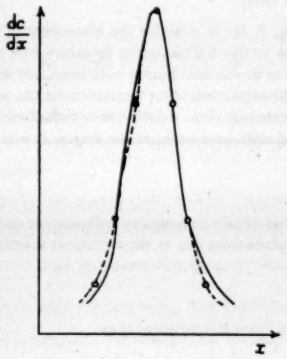

Fig. 3. ——— = experimental sedimentation curve; ----- = corresponding Gaussian curve.

We may now turn to the treatment of the experimental curves corresponding to sedimentation times t_1, t_2, t_3, etc.. We must point out that for the calculation of the breadth of the fraction very short times, i.e., near to the beginning of the experiment, must not be taken, since the start of sedimentation is not very definite in the ultracentrifuge. During the acceleration of the rotor, mixing occurs, but at a certain time sedimentation begins. This time does not generally coincide with that at which the ultracentrifuge has worked up to full speed. Also, in the initial period, when the sedimentation boundary has not yet separated from the meniscus, diffusion occurs only in one direction, i.e., with reflection from the boundary of the liquid. The diffusional broadening will, therefore, be approximately one-half as great as that calculated for free diffusion. We can leave these complications out of account if we take times that are not too near to the start of the experiment. For two times t_1 and t_2 we may then write the difference equation:

$$\frac{1}{\alpha_2^2} - \frac{1}{\alpha_1^2} = 4D(t_2 - t_1) + \frac{(\omega^2 x)^2}{\delta^2}(t_2^2 - t_1^2).$$

From this the required distribution parameter δ^2 can be found.

The calculation is generally carried out for several experimental curves. The scatter of the values of δ^2 found is not great, and the mean value of δ^2, characterizing each fraction, is found. It must be pointed out that in these considerations no arbitrary elements have been admitted. The fundamental integral equation was deduced from the principles of statistics, and it can be solved for the most varied experimental relationships $\frac{dc}{d\xi} = \underline{f}(\xi)$. The fact that our results are closely approximated by means of a Gauss function enables the calculations to be considerably simplified, but is in no way essential to the performance of our scheme of calculation. Table 3 gives the values found for the sedimentation constants s_0, the widths of the distribution curves with respect to sedimentation constants for all of the fractions obtained, and also δ^2, the quantity characterizing the distribution curve $\frac{dc}{ds} = Ke^{-\delta^2(s-s_0)^2}$.

TABLE 3

Experimental Results Relating to Sedimentation Constant Distribution Functions of Polyamides

Polyamide number	Fraction number	Proportion of fraction by weight	Sedimentation constant $\cdot 10^{13}$	Width $\cdot 10^{13}$ of the sedimentation constant distribution curve	Quantity δ^2 characterizing the distribution curve $\cdot 10^{-26}$
1	1 + 2 + 3	0.801	2.1110	1.0000	69.00
	4	0.105	1.8900	0.2640	9.90
	5	0.094	1.5450	0.4670	3.14
2	1	0.280	1.9359	0.2270	13.39
	2 + 3	0.295	1.8407	0.0802	108.00
	4	0.240	1.7080	0.2240	13.75
	5	0.185	0.9979	0.3800	4.67
3	1 + 2	0.598	2.2750	0.0930	79.80
	3	0.317	2.0700	0.3000	7.67
	4	0.085	1.8090	0.3424	5.90
4	1	0.620	1.9070	0.3610	6.70
	2	0.330	1.7986	0.1120	55.30
	3	0.050	1.2930	0.2630	9.96
	2''	0.500	2.3155	0.0704	139.00
	1''	0.500	1.6470	0.3910	4.51

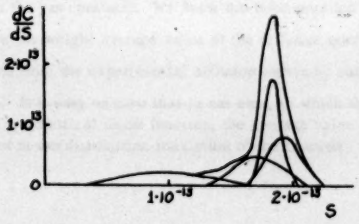

Fig. 4. Sedimentation constant distribution curve for Polyamide Sample No. 1.

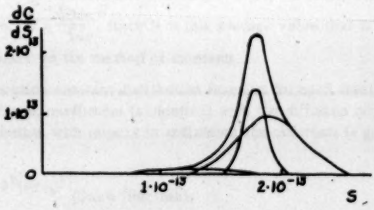

Fig. 5. Sedimentation constant distribution curve for Polyamide Sample No. 2.

In Figures 4 and 5 sedimentation constant distribution curves are constructed from the data so provided.

It must be pointed out here that the fractions obtained by precipitation do not at all fulfill the fundamental requirement of the extensively used method for the construction of differential and summative distribution curves, namely, that the lowest molecular weight for a given fraction must be higher than the highest molecular weight of the preceding fraction. It must, therefore, be concluded that the method of constructing summative and differential distribution curves from fractional precipitation data cannot be regarded as rigorously correct.

SUMMARY

1. A method has been developed for the study of the sedimentation constant distribution function of polymers. It consists in separation of the polymer into a number of fractions by precipitation from solution, followed by the study of each fraction separately by means of ultracentrifuge and diffusion experiments.

2. It has been shown, a number of polyamides being taken as examples, how it is possible to obtain the sedimentation constant distribution function for each fraction by subtraction of the broadening of the sedimentation diagram due to diffusion from the total broadening of the boundary of the sedimenting fraction in the ultracentrifuge.

3. Owing to the fact that the experimental curves for the separate fractions, after correction for the effect of the inhomogeneity of the centrifugal field, are closely approximated by a Gauss function, all of the calculations become extremely simple.

4. By summation of the distribution functions obtained for separate fractions, taking into account the relative weights of the fractions, we may obtain the distribution functions for the whole polymer samples. By this method we have obtained the summative distribution functions for four polyamide samples varying in degree of polycondensation.

Received January 21, 1953

Institute of Macromolecular Compounds and Institute of Organic Chemistry of the USSR Academy of Sciences

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INVESTIGATION BY THE ULTRACENTRIFUGE SEDIMENTATION METHOD OF THE MOLECULAR WEIGHT DISTRIBUTION FUNCTION OF POLYAMIDES

COMMUNICATION 2. MOLECULAR WEIGHT DISTRIBUTION OF POLYAMIDES, AND THE MECHANISM OF POLYCONDENSATION*

S. E. Bresler, V. V. Korshak, S. A. Pavlova, and P. A. Finogenov

Conversion to Molecular Weight Distribution Functions

If the sedimentation constant and diffusion coefficient are known, it is not difficult to determine also the molecular weight of the polymer, since

$$s = \frac{M(1-v\rho)}{f},$$

in which M is the molecular weight; v is the partial specific volume of the polymer; ρ is the specific weight of the solvent; and f is the coefficient of friction, given, according to Einstein's law, by $f = \frac{RT}{D}$, so that $M = \frac{RTs}{D(1-v\rho)}$ (R is the gas constant). We know the sedimentation constant for the distribution maximum of every function, and we know the weight average value of the diffusion coefficient, i.e., $\bar{D} = \frac{\int D dc}{\int dc}$, since it is this average value that is found from the experimental diffusion curves by calculation based on the method of moments.

It is easy to show that in our case, in which the sedimentation constant distribution function for each fraction is a symmetrical Gauss function, the average value of the diffusion coefficient is identical with the diffusion coefficient at the distribution maximum of the fraction. The distribution with respect to sedimentation constants is given by:

$$\frac{dc}{ds} = Ke^{-\delta^2(s-s_0)^2} \text{ (Gauss function)},$$

(s_0 is the most probable sedimentation constant within the given fraction). We may pass from this function to the distribution function with respect to diffusion coefficients if we take into account the fact that the diffusion coefficient is a single-valued function of the sedimentation constant: $D = f(s)$. Since the sedimentation constants within the fraction are close to s_0, then expressing the function f as a series for such values of s and confining ourselves to the first term, we obtain:

$$D - D_0 = \kappa(s-s_0), \text{ in which } \kappa = \left(\frac{df}{ds}\right)_{s=s_0}.$$

Hence, for the distribution function with respect to diffusion coefficients the Gauss function is again valid to the first approximation:

$$\frac{dc}{dD} = K'e^{-\epsilon^2(D-D_0)^2}.$$

In a similar way it can be shown that the molecular weight distribution function is also expressed by a Gauss function. It follows that $D = D_0$, i.e., for every fraction the average diffusion coefficient is the most probable. The diffusion coefficients that we have measured for different fractions may, therefore, be assigned with sufficient accuracy to the "most probable" macromolecules within the fractions, and for these the sedimentation constants have already been determined. From these results, therefore, we may make fully rigorous calculations of molecular weights.

On the basis of these considerations, using the determined values of sedimentation constants and diffusion coefficients, we have calculated the values of the molecular weights of the polyamide fractions investigated (Table 1).

* This paper reports the continuation of work described in Communication 1.

From these data the functional relationships $s = \varphi(M)$ and $D = \varphi'(M)$ can be constructed. It is, however, more rational to present these relationships in an analytical form by the use of the equations of Debye and Kirkwood [1]: $s = KM^n$ and $D = K'M^{1-n}$. According to Debye's equation, the index n depends on the hydrodynamic properties of the macromolecule in solution. If the solvent flows freely past the macromolecule, i.e., if it has a curved thread-like form, $n = 0$, i.e., the sedimentation will cease to depend on the molecular weight. If, on the contrary, the macromolecule is globular and the liquid flows round it, but cannot penetrate it, $n = 0.5$.

TABLE 1

Molecular Weights of Polyamides Determined with the aid of the Ultracentrifuge

Polyamide number	Fraction number	Sedimentation constant · 10^{13}	Diffusion constant · 10^7	Molecular weight
1	1	2.2370	3.8720	40,060
	2	2.1137	5.4470	28,450
	3	2.8780	5.7620	22,440
	4	1.8900	6.0720	22,800
	5	1.5450	13.2360	8,550
	1 + 2 + 3	2.1440	5.0000	31,440
2	1	1.9359	4.8620	29,190
	2	1.7790	5.9400	21,960
	2 + 3	1.8407	5.8200	23,200
	3	1.9200	6.2750	22,430
	4	1.7080	7.1130	17,600
	5	0.9979	23.5000	3,110
3	1	2.5060	2.4310	75,600
	1 + 2	2.2750	3.3760	49,400
	2	2.2040	3.4660	46,600
	3	2.0700	3.6000	42,160
	4	1.7340	7.7870	16,330
4	1	1.9070	5.0870	27,500
	2	1.7986	6.0777	21,700
	3	1.2930	10.8950	8,700
	1''	1.6470	7.5850	15,900
	2''	2.4070	3.0160	58,510

It can be readily shown that our experimental results are closely described by the equation of Debye and Kirkwood. For this purpose it is necessary to plot log s against log M, but it is more convenient to do this for log D and log M, since the difference between the diffusion coefficients for different fractions is greater than that between the sedimentation constants. It is then necessary to pass by calculation from $D = K'M^{1-n}$ to $s = KM^n$, which is readily done with the aid of the known relationship between these three quantities. It will be seen from Figs. 1, 2, and 3 that the dependence of log D on log M is expressed by straight lines. The power index varies somewhat for different samples, but always remains within the limits 0.30-0.33, i.e., the macromolecules of polyamides tend toward a globular form that is not readily penetrated by the solvent. The explanation of this behavior may be that the polyamide chain has a considerable amount of flexibility, owing to the considerable dilution of the peptide linkages by methylene groups.

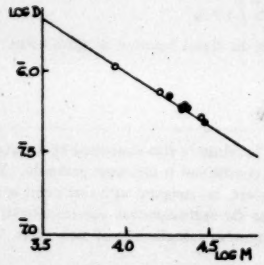

Fig. 1. Dependence of log D on log M: o = for Polyamide No. 4; • = for Polyamide No. 1.

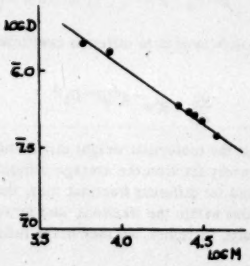

Fig. 2. Dependence of log D on log M for Polyamide No. 2.

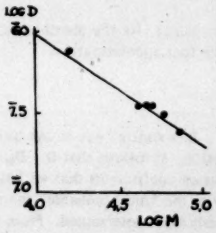

Fig. 3. Dependence of log D on log M for Polyamide No. 3.

We may now readily transform the distribution functions $\frac{dc}{ds} = f(s)$ found above into the required molecular weight distribution functions $\frac{dc}{dM} = \varphi(M)$; for $\frac{dc}{dM} = \frac{dc}{ds} \cdot \frac{ds}{dM} = \frac{dc}{ds} K \cdot n \cdot M^{n-1}$. We shall apply this formula to our experimental results. The relationships found, $D = K' M^{1-n}$ and $s = KM^n$ are given in Table 2.

TABLE 2

Relationships between the Diffusion Coefficient D, the Sedimentation Constant s, and the Molecular Weight for Polyamides

Polyamide number	D	s	ds/dM
1 + 4	$7.08 \cdot 10^{-4} \cdot M^{-0.7}$	$9.657 \cdot 10^{-15} \cdot M^{0.3}$	$2.897 \cdot 10^{-15} \cdot M^{-0.7}$
2	$4.842 \cdot 10^{-4} \cdot M^{-0.67}$	$6.604 \cdot 10^{-15} \cdot M^{0.33}$	$2.179 \cdot 10^{-15} \cdot M^{-0.67}$
3	$5.129 \cdot 10^{-4} \cdot M^{-0.68}$	$6.996 \cdot 10^{-15} \cdot M^{0.32}$	$2.239 \cdot 10^{-15} \cdot M^{-0.68}$

The final molecular weight distribution functions for all of the samples that we have studied are given in Figs. 4, 5, and 6.

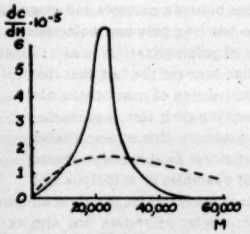

Fig. 4. Experimental molecular weight distribution curve for Polyamide No. 1

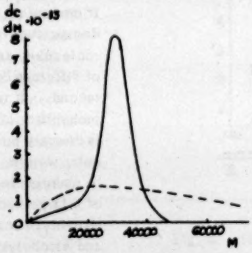

Fig. 5. Experimental molecular weight distribution curve for Polyamide No. 2.

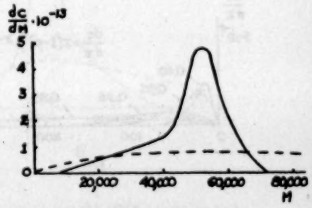

Fig. 6. Experimental molecular weight distribution curve for Polyamide No. 3.

In order to determine the concentrational dependence of the sedimentation constants and diffusion coefficients, special experiments were undertaken. It was found that for all of the polymers studied the concentrational dependence was insignificant, and could not have any appreciable effect on the results of the investigation. For this reason, we carried out all measurements at a standard polymer concentration (0.5%).

Mechanism of Linear Polycondensation, and the Theoretical Molecular Weight Distribution Function

On the basis of our results it is possible to obtain a correct picture of the mechanism of the linear-polymerization reaction. At the present time two views exist on the mechanism of this reaction. One of these, which is widely held in American work, was advanced by Flory [2], and the second was advanced by one of us [3].

Flory regards the process of linear polycondensation as a stepwise reaction of bifunctional molecules, and considers the addition of a monomer molecule to any free functional group (in the case of a polyamide, a carboxyl or amino group) to have the same probability whether the latter belongs to another monomer molecule or is the end group of a polymer chain. Also, Flory regards the already formed polymeric macromolecules as being very stable, being able only to undergo growth as the reaction progresses. The molecular weight distribution function derived by Flory on the basis of these assumptions has the following form:

$$\frac{dc}{dx} = W_x = x(1-p)^2 p^{x-1}$$

(W_x is the fraction by weight of the molecules having a degree of polymerization of x; p is the extent to which the functional groups enter into reaction (progress of reaction). It will be clear that in such a case the number of

molecules of all possible sizes contained in the reaction product can be expressed for any given moment as $N = N_0(1-p)$ (N_0 is the number of monomer molecules). The number of molecules having a degree of polymerization of x will be:

$$N_x = N_0(1-p)\,p^{x-1}$$

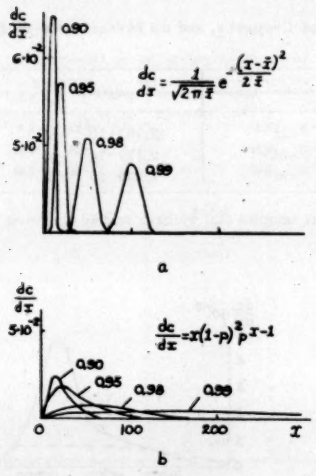

Fig. 7. Molecular weight distribution curves for various values of the progress of reaction: (a) – calculated on the basis of the proposed theory; (b) – calculated from Flory's theory

The characteristic feature of the theory proposed by Flory is the constantly increasing width of the curve expressing the molecular weight distribution function as the extent of polymerization increases, as can be seen from Fig. 7(b). This implies that the polydispersity of polymers will increase enormously with rise in molecular weight.

The other point of view on the mechanism of the linear-polycondensation reaction was advanced by one of us [3], and has been substantiated by numerous investigations. It differs from the first point of view in two fundamental respects: first, it recognizes the major role of exchange, mainly destructive, reactions between polymer and monomer molecules, and also between polymer molecules of different degrees of polymerization; and second, it takes into account the fact that the probability of the destruction of macromolecules is directly proportional to their size, i.e., molecular weight. The tendency of macromolecules to undergo degradation was established in studies of a large number of examples of acidolysis and aminolysis reactions for polyamides [4, 5], acidolysis and alcoholysis reactions for polyesters, and also exchange reactions for polyesters [6] (studied in investigations on polyamidoesters) and various other reactions. In the majority of cases these exchange reactions are destructive and lead to breakdown of already formed macromolecules to shorter ones; and the bigger the molecule, the more bonds it contains that are capable of being broken, and the greater, therefore, is the tendency for such a molecule to undergo degradation. Hence, it is mainly the longest molecules that are degraded.

Owing to the occurrence of these numerous exchange reactions, there is a constant reshuffling of the repeating units in the polymer molecules, and finally a statistical equilibrium molecular weight distribution is established which corresponds to the greatest probability, or entropy. It will be clear that under such circumstances, the molecular weight distribution function will be quite different from that required by Flory's theory. A number of results of this character have already been obtained in studies of the polydispersity of polyamides and polyesters by fractional precipitation from solution [7, 8]. The most reliable results, however, are obtained by means of the ultracentrifuge, which is the ideal apparatus for the study of the polydispersity of macromolecular compounds.

In Figures 4, 5, and 6, we give the distribution curves for the three polyamides No. 1, 2, and 3, as found experimentally by us, and for comparison we show by the broken lines the distribution curves for the same values of the progress of reaction, as calculated from Flory's theory. As will be seen, there is a very great difference between the distribution to be expected on Flory's theory and that actually observed, and this fact must be regarded as a decisive argument against this theory.

Our results again show in very convincing fashion the presence of degradation reactions and their important role in the polycondensation process. This may be illustrated by reference to Polyamide No. 4, which was obtained by heating a mixture of two fractions having molecular weights of 15,000 and 58,000 respectively. Fig. 8 shows the molecular weight distributions for these fractions before heating, and the distribution for the polyamide formed when a mixture of these fractions is heated. The great change produced in the distribution as

a result of the interaction of the fractions will be clearly seen. It is important also to note the close resemblance between the distribution for this polymer, which was not prepared in the usual way, and the distributions for the other three polyamides, which were prepared as usual from the corresponding low-molecular-weight starting materials. It is quite clear that this phenomenon arises solely as the result of degradative exchange reactions.

In order to determine what is to be expected on the basis of the more correct point of view on the mechanism of polycondensation processes, we shall derive a new formula for the distribution function for the case of complete statistical equilibrium in the polycondensation reaction. Since we can always imagine a sequence of secondary reactions (for a given progress of reaction p) such that any monomeric unit will be transferred from an arbitrary position in one polymer chain to an arbitrary position in another, the problem is equivalent to the classical problem of probability theory concerning the distribution of N_0 balls (chain units) into N boxes (macromolecules), all of the events (i.e., the entry of a ball into one or other box) being mutually independent. As is well known, if we denote the number of boxes in which there are x balls by N_x (the number of x-meric macromolecules), we obtain:

$$W_x = N_x x = \frac{x\left(\frac{N_0}{N}\right)^x}{x!} e^{-\frac{N_0}{N}} \approx \frac{1}{\sqrt{2\pi\bar{x}}} e^{-\frac{(x-\bar{x})^2}{2\bar{x}}},$$

(x is the degree of polymerization; W_x is the fraction of x-mers by weight; $\bar{x}$ is the average degree of polymerization of the polymer obtained, and is given by $\bar{x} = \frac{N_0}{N} = \frac{1}{1-p}$). The distribution function, therefore, is expressed by a Gaussian curve, the half-width of which, measured at the middle point of its height, will be given by:

$$\Delta x = (x - \bar{x})_0 = \sqrt{2 \cdot \ln 2 \cdot \bar{x}} \approx \sqrt{1.4\bar{x}}$$

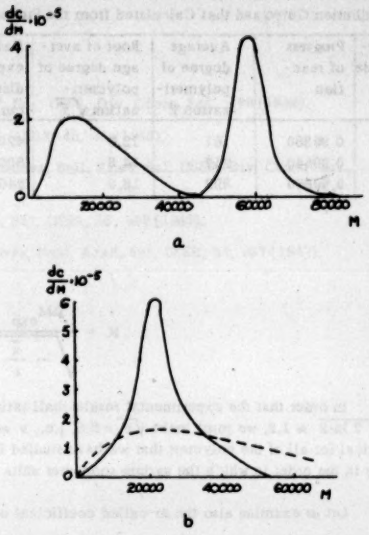

Fig. 8. Molecular weight distribution curves: (a) – for two fractions of mixed polyamide; (b) – for the same, after being mixed and heated together.

Such curves, calculated for various values of p from 0.9 to 0.99 are given in Fig. 7(a). It will be seen that they are indeed quite different from the Flory curves. As the extent of polycondensation increases, the breadth of the distribution increases comparatively little, proportional, in fact, to $\sqrt{\frac{1}{1-p}}$.

In Table 3 we give the experimentally found proportionality coefficients, calculated as

$$K = \frac{\Delta M_{exp}}{\sqrt{\bar{x}} \cdot 113} = \frac{\Delta x_{exp}}{\sqrt{\frac{1}{1-p}}}$$

(ΔM_{exp} is the half-width of the experimental molecular weight distribution curve measured at half-height; 113 is the weight of the repeating unit).

The proportionality coefficient K can be regarded as practically constant for all of the three values of the progress of reaction. Hence, as the theory of the statistical equilibrium distribution predicts, the breadth of the curve increases proportionally to the root of the average degree of polymerization of the sample. At the same time, the absolute value of the coefficient K is about 2.5 times as great as that calculated from the theory. This indicates that a definite correlation exists between the closest units of the polyamide chain, i.e., that any particular unit cannot occupy, independently of others, any position in any macromolecule. One of the sources of such correlation is clear.

TABLE 3

Relation between the Experimental Half-width of the Molecular Weight Distribution Curve and that Calculated from the Proposed Formula

Polyamide No.	Progress of reaction	Average degree of polymerization $\bar{x}$	Root of average degree of polymerization $\sqrt{\bar{x}}$	Half-width of expt. mol. wt. distribution curve	Proportionality coefficient K
2	0.99380	161	12.6	4200	2.95
1	0.99540	217	14.8	5000	2.99
4	0.99690	322	18.0	6400	3.14

The essential point is that immediately after a diamine unit a dicarboxylic acid unit is bound to occur, so that the correlation between the two adjacent units is obvious. Let us suppose that the correlation extends over ν consecutive units. Mathematically this means that the size of the elementary unit has grown by a factor of ν, and the total number has been correspondingly reduced by a factor of ν. Hence:

$$K = \frac{\Delta M_{exp}}{\sqrt{-\frac{\bar{x}}{\nu}} \cdot 113\nu} = \frac{\Delta M_{exp}}{\sqrt{\bar{x}\nu} \cdot 113}$$

In order that the experimental results shall satisfy the theoretical relationship, according to which $K = \sqrt{2 \ln 2} \approx 1.2$, we must make $\sqrt{\nu} = 2.5$, i.e., $\nu \approx 6$. The fact that the value of ν is greater than two and is identical for all of the polymers that we have studied indicates that in a mixed polymer there is a certain regularity in the order in which the various monomer units occur.

Let us examine also the so-called coefficient of polydispersity $\frac{M_w}{M_c}$ (M_w is the weight average molecular weight, and M_c is the number average molecular weight). With increase in the progress of reaction, experiment shows that $\frac{M_w}{M_c}$ falls and tends to unity. The same conclusion follows from our theory for the equilibrium distribution. According to Flory, on the other hand, the coefficient of polydispersity should rise as the average molecular weight of the product increases, and it should tend to the value of two.

The results of this investigation, therefore, are in direct conflict with the theory that regards polycondensation as simple stepwise chain growth. It follows from our results that the polycondensation process proceeds as a complex system of destructive and synthetic reactions, in the course of which the growing polymer molecules continually interact among themselves and with the molecules of the starting materials. As a result, the molecular weight distribution attained is close to an equilibrium one.

SUMMARY

1. Sedimentation constants and diffusion coefficients have been determined in the ultracentrifuge for four samples of polyamides.

2. On the basis of these examples a fairly rigorous method has been developed for the determination of the molecular weight distribution function for polymers.

3. The experimentally obtained distribution functions have been compared with the theoretical curves required by Flory's theory, and the invalidity of this theory has been demonstrated.

4. The results obtained are explained as a consequence of the occurrence, durin g the polycondensation process, of exchange and degradation reactions between the polymer molecules themselves and between polymer and monomer molecules; as a result of these reactions, the distribution function obtained is fairly narrow.

5. It is pointed out that the widely used methods, based on precipitation from solution, for the fractionation of polymers and the determination of their molecular weight distribution are unsatisfactory.

6. It is concluded that, in solution, polyamides behave as if they consist of compact, not readily penetrated, globular particles; which is an indication of the considerable flexibility of their chains.

Received January 21, 1953

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SOME REACTIONS OCCURRING DURING THE POLYMERIZATION OF BUTYL VINYL ETHER

M. F. Shostakovsky and V. A. Gladyshevskaya

The study of the polymerization processes of alkyl vinyl ethers is of considerable interest owing to the fact that these compounds comprise a large group of polymerizable substances of particularly high reactivity. The high chemical activity of these compounds is dependent on the presence of a double bond in immediate proximity to the ether oxygen [1]. Owing to this structural peculiarity, the properties of the double bond of a vinyl ether are greatly different from those of the double bonds of many compounds that may be included under the general heading of ethylene derivatives. The high reactivity of alkyl vinyl ethers comes into particular prominence in studies of ionic polymerization and copolymerization processes [2].

Vinyl ethers form one of the classes of compounds that can react both by the ionic and by the free-radical mechanism [3]. According to the nature of the catalysts used in the polymerization of alkyl vinyl ethers, the mechanism of the process that occurs will be ionic or free-radical in type. A number of catalysts, such as mineral acids, metal chlorides, and halogens [4, 5, 6, 7], induce the polymerization of vinyl ethers by an ionic process [3]. The course of the process is determined by the properties of the catalyst and the temperature.

As our previous investigations have shown, polymerization processes occurring under the catalytic action of $FeCl_3$ and HCl proceed most smoothly at a temperature close to the boiling point of the vinyl ether [8].

In this connection it may be assumed that at the boiling point of the vinyl ether, decomposition of the intermediate complex(I) occurs with formation of an active molecule of the vinyl ether (II), which initiates a propagating polymer chain (III) [9]:

$$CH_2{=}CHOR + HCl \longrightarrow CH_2{=}CHOR{\cdot}HCl \qquad (I)$$

$$CH_2{=}CHOR{\cdot}HCl \longrightarrow CH_3\overset{+}{C}HOR + Cl' \qquad (II)$$

$$CH_3\overset{+}{C}HOR + n\,CH_2{=}CHOR \longrightarrow CH_3CH[CH_2{-}\underset{\underset{OR}{|}}{CH}]_{n-1}{-}CH_2{-}\overset{+}{\underset{\underset{OR}{|}}{C}}H{-} \qquad (III)$$

Termination of the ionic polymer chain may occur in various ways. There are indications in the literature [10] that the termination of polymer chains may occur by the action of traces of impurities, such as alcohols.

We have already pointed out the importance of the purity of alkyl vinyl ethers in polymerization processes [11]. The main impurities found in alkyl vinyl ethers are the alcohols employed as starting materials in the preparation of the ethers. Alcohols present in the original vinyl ethers take part in chain-termination reactions, leading to the formation of low-molecular-weight compounds. Also, alcohols readily react with the original alkyl vinyl ethers, forming acetals [12]. A study, however, of the composition and structure of the resulting acetals is not sufficient for the elucidation of the part played by alcohols in the polymerization process. We have therefore undertaken the present investigation in order to elucidate further the action of alcohols, which have been introduced into the reaction mixture at various times during the polymerization.

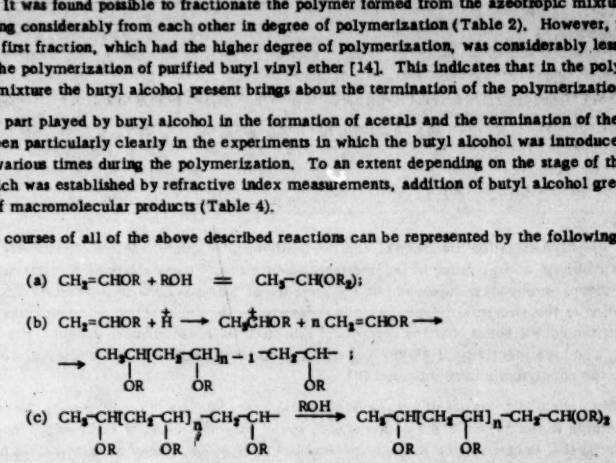
In the present investigation we have studied the reactions of mixtures of butyl vinyl ether and butyl alcohol. First of all we studied a mixture of 92% of butyl vinyl ether and 8% of butyl alcohol, which is an azeotropic mixture [13]. In the investigation of the chemical reactions of such mixtures, the question of the possibility of obtaining reproducible results is of great interest. For this purpose a series of experiments was carried out in which standard conditions were observed, and the products were characterized by determinations of viscosity (1 g of the substance in 100 ml of benzene), refractive index, and molecular weight. As a result of this work, it was found possible to obtain products that were very closely alike with respect to their constants in all of the experiments (Table 1).

As a result of further treatment of the products, it was shown that reaction proceeded in several directions in the mixture, the final result being the formation of acetaldehyde dialkyl acetal, polymer, and possibly other

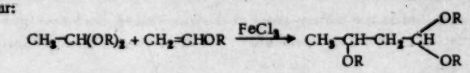
substances. It was found possible to fractionate the polymer formed from the azeotropic mixture into two fractions differing considerably from each other in degree of polymerization (Table 2). However, the molecular weight even of the first fraction, which had the higher degree of polymerization, was considerably less than that of the product of the polymerization of purified butyl vinyl ether [14]. This indicates that in the polymerization of the azeotropic mixture the butyl alcohol present brings about the termination of the polymerization process.

The part played by butyl alcohol in the formation of acetals and the termination of the polymerization process is seen particularly clearly in the experiments in which the butyl alcohol was introduced into the reaction mixture at various times during the polymerization. To an extent depending on the stage of the polymerization process, which was established by refractive index measurements, addition of butyl alcohol greatly impeded the formation of macromolecular products (Table 4).

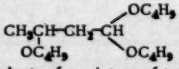
The courses of all of the above described reactions can be represented by the following schemes:



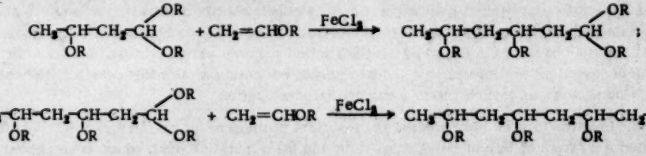
It was found, however, that the polymerization processes of alkyl vinyl ethers containing additions of various alcohols are even more complicated than those represented in the above schemes. In these no account is taken of the fact that an extremely active new substance, the acetal of the corresponding alcohol, is formed. This compound, we consider, has a mobile hydrogen, and as a result, reaction in the following direction may readily occur:



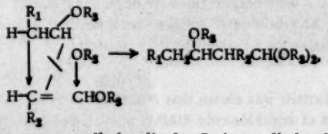
(R is alkyl).


– (1,1,3-tributoxybutane) was isolated, together with the acetal, from the reaction products of a mixture of two molecular proportions of butyl vinyl ether and one of butyl alcohol. In this process a polymer of very low molecular weight (564) was also formed.

The formation of 1,1,3-tributoxybutane by the reaction of the acetal with the alkyl vinyl ether is very interesting, since, as a further development of the idea of reaction between 1,1,3-tributoxybutane, we may postulate gradual growth of the chain, proceeding as follows:



i.e., the chain grows as a result of step-by-step polymerization. This does not exclude, however, the possibility of a second mechanism of chain growth, represented in a paper by Hoaglin and Hirsh [15] as follows:



(R_1 and R_2 are hydrogen atoms or alkyl radicals; R_3 is an alkyl radical).

It may be assumed also that the low-molecular-weight polymer isolated in the described transformations may be formed in the following two ways: 1) ionic chain polymerization; 2) stepwise polymerization. In its molecular weight it corresponds to 1,1,3,5,7-pentabutoxyoctane.

These suppositions, and also the experimental proof of the true mechanism of the reactions described, will form the object of our further investigations.

The formation of 1,1,3-trialkoxybutanes is described in the paper of Hoaglin and Hirsh [15], but they do not characterize 1,1,3-tributoxybutane, which we isolated from the reaction products of the mixture of two molecular proportions of butyl vinyl ether and one molecular proportion of butyl alcohol; in the present investigation we have therefore carried out a special synthesis of 1,1,3-tributoxybutane.

It has therefore been established that, when alkyl vinyl ethers contain alcohols, the latter play an important part in many ways in the course of the polymerization process. The presence of an alcohol in the reaction mixture may lead to the occurrence of various chemical reactions that will greatly affect the composition and properties of the products.

EXPERIMENTAL

1. Starting Materials. With a view to their purification, the starting materials were treated as follows:

a) Butyl alcohol was washed with dilute sulfuric acid and with sodium bisulfite solution, and was boiled for 90 minutes with a 20% solution of caustic soda. It was then washed with water, dried over potassium carbonate and then over barium oxide, and then distilled from a flask fitted with a Vigreux column [16]. After purification in this way, the butyl alcohol had the following constants: b.p. 117.6° (760 mm); n_D^{20} 1.3995; d_4^{20} 0.8100; η 2.816 centipoise.

b) Butyl vinyl ether (commercial product) was purified by washing five times with equal volumes of water, drying, and treating with sodium. The ether was then distilled, and for the experiments the fraction of b.p. 93.5° was taken; it had the following constants: n_D^{20} 1.4026; d_4^{20} 0.7795; η 0.439 centipoise.

From these components two mixtures were made: 1) the azeotropic mixture (92% of butyl vinyl ether and 8% of butyl alcohol); and 2) a mixture of two molecular proportions of butyl vinyl ether and one of butyl alcohol.

c) The catalyst used was a 5% solution of ferric chloride in absolute butyl alcohol.

2. Study of the Reactions of the Azeotropic Mixture of Butyl Vinyl Ether and Butyl Alcohol. The reaction was carried out in a three-necked round-bottomed flask fitted with mercury-sealed mechanical stirrer and reflux condenser. The azeotropic mixture (100 g) was poured into the flask and heated to 95-97°. At this temperature catalyst was added in small portions (0.04 g) at a time. As each portion of catalyst was added, the temperature of the reaction mixture rose. Addition of catalyst was discontinued when its addition caused no temperature rise, thus indicating that reaction was complete. In the course of the experiment, altogether 0.24 g of catalyst was added. The experiment lasted for two hours. Further experiments (Table 1, Expt. No. 4) showed that reduction of the total amount of catalyst to 0.06 g had no effect on the final result of the process so long as it was all added at once and the duration of the reaction was increased to four hours.

By observance of the above-described conditions, it was found possible to obtain products that were closely alike with respect to their constants in all of the experiments (Table 1).

TABLE 1

Constants of Products Obtained by Reaction of an Azeotropic Mixture of Butyl Vinyl Ether and Butyl Alcohol

Expt. No.	n_D^{20}	d_4^{20}	Viscosity of soln. of 1 g polymer in 100 ml benzene (centipoise)	Yield (%)
1	1.4455	0.9043	0.676	95
2	1.4460	0.9048	0.676	94
3	1.4455	0.9038	0.676	96
4	1.4460	0.9045	0.676	95

The viscosity of a solution of 1 g of the polymer in 100 ml of benzene was determined with an Ostwald viscosimeter at 20°.

The reaction products were distilled under reduced pressure, and the macromolecular products were suitably purified. Vacuum fractionation of 50 g of the isolated product yielded:

Fraction I, b.p. 68° (8 mm), 7 g
Residue 41 g

Refractionation of Fraction I under normal pressure from a flask having a

Vigreux column yielded a substance having the following constants: b.p. 185-186 (760 mm); n_D^{20} 1.4090; d_4^{20} 0.8255. For acetaldehyde dibutyl acetal, the literature [11] gives: b.p. 184-185° (760 mm); n_D^{20} 1.4090; d_4^{20} 0.8267.

The constants cited therefore indicate that the substance was the dibutyl acetal, which has already been prepared several times. The residue was a light-yellow polymer; before reprecipitation, it had the following constants: n_D^{20} 1.4560; d_4^{20} 0.9287; η 0.684 centipose; M 1439.

This polymer was reprecipitated: A solution of the polymer (30 g) in diethyl ether (120 ml) was filtered, and ethanol (240 ml) was added; no precipitation of polymer occurred. Distilled water (30 ml) was then added cautiously to the solution. The solution rapidly became turbid, and polymer gradually separated. The latter was separated from the solvents, which were then distilled, yielding, as residue, a second polymer fraction. In order to purify them further, the polymer fractions were heated at 90-100° under low pressure (15 mm) for six hours. The characteristics of the resulting fractions are given in Table 2.

TABLE 2

Characteristics of Polymer Fractions Obtained by Reprecipitation

Fraction No.	Molecular weight determined cryoscopically in benzene	n_D^{20}	Viscosity of soln. of 1 g polymer in 100 ml benzene (centipoise)	Yield (%)
1	2112	1.4600	0.701	74
2	682	1.4500	0.653	18

TABLE 3

Variation of the Refractive Index of the Reaction Mixture during the Polymerization of Butyl Vinyl Ether

Temp. of reaction mixture (°C)	n_D^{20}	Note
97	1.4060	Refractive index measurements were made at 20-min. intervals. At the end of the experiment, the resulting polymer had n_D^{20} 1.4560.
97	1.4080	
97	1.4120	
97	1.4220	
97	1.4320	
104	1.4420	
104	1.4480	
104	1.4520	
104	1.4540	
104	1.4560	
97	1.4560	

3. Investigation of the Conditions for the Termination of the Polymerization Processes of Butyl Vinyl Ether by Addition of Butyl Alcohol during the Polymerization. The procedure described in Section 2 was employed. We made preliminary observations on the course of the polymerization process, which was followed by the changes occurring in the refractive index of the reaction mixture. Refractive index measurements were made at 20-minute intervals. The results are given in Table 3.

In the course of these investigations we selected four points at which to make additions of butyl alcohol, namely, when the refractive index of the mixture attained the following values: 1.4120, 1.4220, 1.4320, 1.4420. In every experiment, as soon as the refractive index attained the required value, 74 g of butyl alcohol was added to the reaction mixture. After this the experiment was continued for a further two hours.

The products were vacuum-fractionated, and two main fractions were isolated: the first having b.p. 41-43° (15 mm), and the second b.p. 80-82° (15 mm). After the fractionation macromolecular products remained in the flask. Further fractionations of the fractions yielded two substances. The first had the following constants: b.p. 117-118° (760 mm); n_D^{20} 1.3990; d_4^{20} 0.8106; which identifies it with butyl alcohol, for which the literature gives [13]: b.p. 117.6-117.7°; n_D^{20} 1.3997; d_4^{20} 0.8095.

The second compound had b.p. 185-186° (760 mm); n_D^{20} 1.4087, d_4^{20} 0.8262.

These constants correspond to the dibutyl acetal $CH_3CH(OC_4H_9)_2$ [12]. All of the results obtained in these experiments are summarized in Table 4.

TABLE 4

Characteristics of Products Obtained by Termination of the Polymerization Process by Means of Butyl Alcohol

Expt. No.	n_D^{20} of reaction mixture at which butyl alcohol added	Amounts of substances obtained in fractionation (%)			Refractive indices of polymers obtained
		Butyl alcohol	Dibutyl acetal	Polymer	
1	1.4120	26.5	59	11.5	1.4165
2	1.4220	33.2	44.5	17.4	1.4360
3	1.4320	34.6	39.2	20.2	1.4520
4	1.4420	36.5	30.7	30.2	1.4580

4. Study of the Reactions of a Mixture of Two Molecular Proportions of Butyl Vinyl Ether and One of Butyl Alcohol. The mixtures investigated contained 37 g of butyl alcohol to 100 g of butyl vinyl ether. The procedure was as described in Section 2. The experiments yielded light-yellow products of low viscosity. Vacuum fractionation of such a product (50 g) yielded:

Fraction I	b.p. 68- 72° (8 mm),	29.5 g
Fraction II	b.p. 75-135° (8 mm),	0.4 g
Fraction III	b.p. 135-138° (8 mm),	5.5 g
Residue		13.8 g

Fraction I, after purification by further fractionation, had the following constants: b.p. 186-187° (760 mm); n_D^{20} 1.4088; d_4^{20} 0.8258. It follows from these constants that it was the dibutyl acetal [12].

Fraction III was again fractionated under reduced pressure, and it yielded a product of b.p. 137-138° (8 mm) and having the following constants: n_D^{20} 1.4259; d_4^{20} 0.8661, found MR 81.04; calculated $C_{16}H_{34}O_3$ MR 81.017.

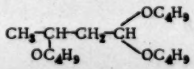
Found: M 266

$C_{16}H_{34}O_3$. Calculated: M 274

Found %: C 69.76, 69.60; H 12.45; 12.38

$C_{16}H_{34}O_3$. Calculated %: C 70.00 H 12.49

From these results we concluded that the substance was 1,1,3-tributoxybutane –



The residue in the flask (not reprecipitated) had the following constants: n_D^{20} 1.4480; d_4^{20} 0.9073; M 564; η 0.646 centipoise. It was a low-molecular-weight polymer of butyl vinyl ether.

5. Synthesis of 1,1,3-Tributoxybutane. To 174 g (1 mole) of acetaldehyde dibutyl acetal, 4 g of a 5% solution of ferric chloride in butyl alcohol was added. The mixture was stirred and heated in a flask in a water bath at 48°. Butyl vinyl ether (50 g, i.e., 0.5 mole) was then added dropwise, the rate of addition being regulated so that the temperature remained in the range 48-50°. After the whole of the ether had been added, the experiment was continued for one hour further. The catalyst was then neutralized with anhydrous sodium carbonate powder (5 g). The mixture was stirred for three hours, and then filtered. The product was 215 g of a colorless liquid. Vacuum fractionation yielded:

Fraction I	b.p. 40- 70° (8 mm),	130 g
Fraction II	b.p. 80-140° (8 mm) (major portion at 138°),	62 g
Fraction III	b.p. 145-195° (8 mm),	10 g
Residue		7 g

Fraction I, after purification by refractionation, had the following constants: b.p. 184-185° (754 mm); n_D^{20} 1.4084; d_4^{20} 0.8270. It therefore consisted of the dibutyl acetal [12].

Fraction II, after refractionation, had the following constants: b.p. 137-138° (8 mm); n_D^{20} 1.4255; d_4^{20} 0.8655; found MR 81.02, calculated $C_{16}H_{34}O_3$ MR 81.017.

Found: M 289.9
$C_{16}H_{34}O_3$. Calculated: M 274

Found %: C 70.09; 70.33; H 12.57, 12.49
$C_{16}H_{34}O_3$. Calculated %: C 70.00 H 12.49

These constants fully confirm the identity of Fraction II with the 1,1,3-tributoxybutane isolated from the product obtained by the polymerization of butyl vinyl ether in presence of butyl alcohol.

In the present investigation, we have not studied Fraction III and the residue.

SUMMARY

1. From reaction products obtained from mixtures of butyl vinyl ether and butyl alcohol, three substances have been isolated: acetaldehyde dibutyl acetal, 1,1,3-tributoxybutane, and polymer.

2. Two polymer fractions, characterized by molecular weight, viscosity in benzene solution, and refractive index, have been obtained.

3. It has been shown that the degree of polymerization can be regulated by addition of butyl alcohol during the polymerization of butyl vinyl ether.

4. 1,1,3-Tributoxybutane has been prepared by the reaction of acetaldehyde dibutyl acetal with butyl vinyl ether.

Received January 3, 1953

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• See Consultants Bureau Translation, page 105.

EFFECT OF PRESSURE ON THE MECHANISM OF THE THERMAL CRACKING OF PARAFFINS

M. G. Gonikberg and V. V. Voevodsky

In this paper we shall attempt to reach some conclusions concerning the mechanism of the cracking of paraffins from an analysis of experimental data on the relation between the rate of cracking and the pressure. Until recently these data have been confined to a short range of pressures (not above 25 atm.). It has been established that at moderate pressures (a few atmospheres), the rate of cracking generally increases with increase in pressure (the decompositions of ethane at 750° and 800° [1], propane at 600° [2], butane at 575° [3] and 600° [2], and heptane at 580° [4]); only in one investagation [5] was a retardation of cracking observed (ethane at 635°). It should be pointed out that the thermal decomposition of butane is intensified by increase of pressure up to a value of 10 atm, but further increase of pressure up to 25 atm has no essential effect on the rate of the process [3].

The cause of the acceleration of the cracking of paraffins by increase in pressure has been attributed by a number of authors to the simultaneous occurrence of decomposition reactions proceeding according to unimolecular and bimolecular schemes. Thus, for the decomposition of ethane the following reactions have been proposed [3]:

$$C_2H_6 = C_2H_4 + H_2.$$

$$2C_2H_6 = 2CH_4 + C_2H_4.$$

and the acceleration of cracking by increase in pressure has been explained by the acceleration of the bimolecular reaction (the second).

It has been recently established, however, that high pressure (of the order of hundreds and thousands of atmospheres) does not accelerate, but, on the contrary, retards the cracking of paraffins.

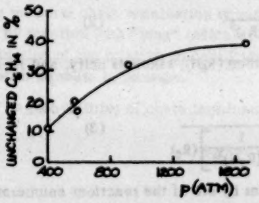

Fig. 1. Effect of pressure on the progress of the thermal cracking of hexane at 430° (τ = 3 hr.)

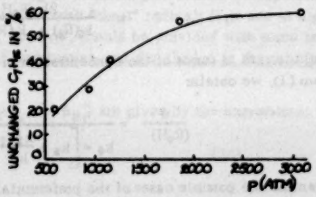

Fig. 2. Effect of pressure on the progress of the thermal cracking of heptane at 420° (τ = 3 hr.)

Figures 1 and 2 show the results of an investigation [6] of the thermal cracking of hexane at 430° and at pressures of 390-1680 atm., and of heptane at 420° and 620-3100 atm; these indicate the great increase in the proportion of unchanged hydrocarbon at the high pressures. It was shown also that the observed retardation of cracking could not be accounted for by the displacement of a chemical equilibrium. Similar conclusions may be drawn also from recent work on the thermal cracking of propane at 600° and at 98 and 197 atm., and of butane at 550° and at pressures of 104 and 172 atm. [7]. It should be noted also that with increase in pressure the yield of low-boiling cracking products is reduced, and there is an increase in the relative content of the higher-boiling (in comparison with the original) hydrocarbons [6].

Thus, at moderate pressures (a few atmospheres) cracking is generally accelerated by increase in pressure,

and at high pressures (hundreds and thousands of atmospheres) it is retarded. Let us examine whether a chain mechanism for the decomposition of the paraffin R_0H is consistent with these conditions.

Let us assume, as is usual, that the initiation of chains results from the breakdown of an R_0H molecule into radicals that are shorter in length, and these react with a molecule of the original hydrocarbon with formation of R_0 radicals:

$$R_0H \xrightarrow{k_1} R' + R'' \xrightarrow{+\,2R_0H} 2R_0 + R'H + R''H \qquad (a)$$

The radical R_0 may either break down with formation of a shorter radical R_1 and an olefin O 1, or react with an olefin molecule and form a longer radical R_2:

$$R_0 \xrightarrow{k_2} R_1 + O1 \qquad (b)$$

$$R_0 + O1 \xrightarrow{k_3} R_2 \qquad (c)$$

The resulting radicals may react in their turn with molecules of the original hydrocarbon, and so continue the chain; for example:

$$R_1 + R_0H \xrightarrow{k_4} R_0 + R_1H. \qquad (d)$$

[see the right-hand side of the equation (a)].

Finally, chain termination may occur either at the wall (k_5), or by reactions (recombination or disproportionation) of the radicals R_0 and R_1 ($R_0 + R_0 - k_6$; $R_0 + R_1 - k_7$; $R_1 + R_1 - k_8$).

We exclude from consideration all reactions associated with the formation of the longer (in comparison with the original hydrocarbon) radicals R_2 and their further reaction. These reactions appear to play an important part in the cracking of paraffins to which olefins have been added, but they cannot form the main chain-breaking process in absence of additions, particularly at high pressures [8].

Under stationary conditions, when the length of the chain is considerable:

$$k_2(R_0) = k_4(R_1)(R_0H) \qquad (1)$$

(the parentheses indicate concentrations). The rate of chain initiation is $2k_1(R_0H)$. We shall now write an expression for the reaction rate w equal to the product of the rate of initiation of chains and the rate of their growth, divided by the rate of chain termination:

$$w = \frac{2k_1(R_0H) \cdot k_4(R_1)(R_0H)}{k_5(R_0) + k_6(R_0)^2 + k_7(R_1)(R_0) + k_8(R_1)^2}. \qquad (2)$$

Expressing the rate in terms of the concentration of the original hydrocarbon (R_0H), taken as unity, and substituting for R_1 from (1), we obtain:

$$\frac{w}{(R_0H)} = \frac{2k_1k_2}{k_5 + \left[k_6 + \frac{k_2k_7}{k_4} \cdot \frac{1}{(R_0H)} + \frac{k_2^2k_8}{k_4^2} \cdot \frac{1}{(R_0H)^2}\right](R_0)} \qquad (3)$$

Let us examine the possible cases of the preferential termination of chains by one of the reactions enumerated.

a) Chain termination occurs preferentially at the walls, when:

$$\frac{w}{(R_0H)} = \frac{2k_1k_2}{k_5} \qquad (4)$$

i.e., the reaction rate (in the units indicated) is independent of the pressure (if we neglect the effect of pressure on the rate constants k_1, k_2, and k_5).

b) Chain termination occurs preferentially on radicals of the original hydrocarbons:

$$\frac{w}{(R_0H)} = \frac{2k_1k_2}{k_6(R_0)} \qquad (5)$$

From the condition for a stationary state we find:

$$2k_1(R_0H) = k_6(R_0)^2 \qquad (6)$$

From (5) and (6) we obtain:

$$\frac{w}{(R_0H)} = \sqrt{\frac{2k_1}{k_6}}\, k_3(R_0H)^{-\frac{1}{2}} \qquad (7)$$

i,e., the reaction rate falls with increase in (R_0H): the reaction is retarded by increase in pressure.

c) Chain termination occurs preferentially on the short radicals R_1:

$$\frac{w}{(R_0H)} = \frac{2k_3k_4^2}{k_2k_6} \cdot \frac{(R_0H)^2}{(R_0)}. \qquad (8)$$

From the condition for a stationary state we find:

$$2k_1(R_0H) = k_6(R_1)^2. \qquad (9)$$

From (1), (8), and (9) we obtain:

$$\frac{w}{(R_0H)} = \sqrt{\frac{2k_1}{k_6}}\, k_4 \cdot (R_0H)^{\frac{1}{2}} \qquad (10)$$

i,e., the reaction rate rises with increase in (R_0H): the reaction is accelerated by increase in pressure.

d) Chain termination occurs preferentially by the interaction of the radicals R_0 and R_1:

$$\frac{w}{(R_0H)} = \frac{2k_1k_4}{k_7} \cdot \frac{(R_0H)}{(R_0)}. \qquad (11)$$

From the condition for a stationary state we find:

$$2k_1(R_0H) = k_7(R_0)(R_1). \qquad (12)$$

From (1), (11), and (12) we obtain:

$$\frac{w}{(R_0H)} = \sqrt{\frac{2k_1k_2k_4}{k_7}}. \qquad (13)$$

i,e., the reaction rate is independent of pressure.

The data cited above concerning the effect of pressure on the rate of cracking and the analysis of various cases of the preferential termination of chains in the thermal cracking of paraffins give reason to suppose that at moderate pressures chain termination occurs preferentially by reaction with "short" radicals (R_1), and at high pressures by reaction with "long" radicals (R_0). This supposition, however, should be provided with some basis by an examination of the relative probabilities of these two types of termination and the change in the relative probability with increase in pressure.

The probabilities of chain termination on R_0 and on R_1 (δ_{R_0} and δ_{R_1}) are given by the expressions:

$$\delta_{R_0} = \frac{k_6(R_0)^2}{k_2(R_0)} = \frac{k_6}{k_2}(R_0) \qquad (14)$$

and

$$\delta_{R_1} = \frac{k_6(R_1)^2}{k_6(R_1)(R_0H)} = \frac{k_6(R_1)}{k_6(R_0H)} \qquad (15)$$

It follows from (1) that:

$$\frac{(R_0)}{(R_1)} = \frac{k_4}{k_2}(R_0H),$$

so that

$$\frac{\delta_{R_0}}{\delta_{R_1}} = \frac{k_4^2k_6}{k_2^2k_6}(R_0H)^2. \qquad (16)$$

The ratio of the probabilities of termination on R_0 and on R_1 is therefore proportional to the square of the concentration of the original hydrocarbon. In other words, this ratio increases very rapidly with rise in pressure, which is a qualitative confirmation of the supposition made above.

An approximate quantitative examination of this question also leads to the conclusion that an increase in pressure of, say, from 5 to 500 atm. may result in the change indicated in the process of chain termination. Let

us find the orders of magnitude of the rate constants entering into the expression (16):

$$\frac{\delta R_2}{\delta R_1} \approx \frac{f_4^2 f_6}{f_2^2 f_3} \left(10^{-23} e^{\frac{E_2 - E_4}{RT}} \cdot \frac{10^{19}}{T} \cdot 760 \cdot P_{R_0H} \right)^2 .$$

(f_2, f_4, f_6, and f_3 are the steric factors of the corresponding reactions; T is the absolute temperature; P_{R_0H} is the pressure of the hydrocarbon (atm).

The activation energies E_2 and E_4 can be approximately evaluated from the energy of rupture of a C–C bond into free radicals [9, 10]:

$$E_2 \approx 12-20 \text{ kcal/ mole}$$

and from data concerning the kinetics of the reactions

$$CH_3 + RH \longrightarrow CH_4 + R \text{ [11]:}$$

$$E_4 \approx 7-8 \text{ kcal/mole.}$$

Values of $\delta R_0/\delta R_1$

p(atm)	E_2-E_4 (kcal/mole)	
	5,000	12,000
5	$3.7 \cdot 10^{-4} F$	$8.3 F$
500	$3.7 F$	$8.3 \cdot 10^{4} F$

Substituting T = 700°K we find the values of $\delta R_0 / \delta R_1$ given in the table (for extreme values of the difference E_2-E_4).

The value of $F = \frac{f_4^2 f_6}{f_2^2 f_3}$ can be roughly evaluated from the following data:

$$\frac{f_6}{f_3} \approx 10^{-3} - 10^{-5} ,$$

since the recombination of "long" radicals is considerably hindered sterically.* The value of f_4 may be taken to be about 10^{-3}, by analogy to $CH_3 + RH$ reactions [13]. The values of f_2 for the rupture of C–C bonds in free radicals are very low, being about $10^{-4} - 10^{-5}$ [10]. Hence, accurate within a factor of ten, we may write:

$$F \approx 10^{-2} \left(\frac{10^{-3}}{10^{-4}} \right)^2 \approx 1.$$

It will be seen from this approximate calculation that, for a very extensive range of values of the difference E_2-E_4, the ratio $\delta R_0/\delta R_1$ may change from values $\ll 1$ to values $\gg 1$ as we pass from 5 to 500 atm. The variation of the kinetics of the thermal cracking of paraffins with rise in pressure may therefore be explained by a change in the nature of the predominant chain-terminating reaction.

In the above analysis we have excluded from consideration the reaction (c), which leads to the formation of radicals of higher molecular weight than that of the original hydrocarbon (i.e., the alkylation reaction), and also the subsequent reactions of these radicals. It is natural to suppose that the alkylation of paraffins by olefins, with formation of substances higher in molecular weight than the original substances, will be considerably accelerated by increase in pressure. In the case we have considered these reactions therefore have a modifying effect on the retardation produced by high pressure on thermal cracking. In the absence of alkylation reactions, this retarding effect of pressure would be much more strongly marked.

Actually, the results of one of the investigations cited [6] show that under a hydrogen pressure of about 200 atm. the alkylation and polymerization reactions occurring in the cracking of hexane and heptane are suppressed owing to the hydrogenation of the olefins [14], and this results in a considerable reduction in the rate of cracking, as measured by the proportion of unchanged original hydrocarbon. However, further increase in the hydrogen pressure to 1200 atm. [6] results in the acceleration of thermal decomposition. This is probably due to participation of hydrogen in chain propagation, according to the scheme:

$$R_1 + H_2 = R_1H + H,$$

$$H + R_0H = R_0 + H_2.$$

A similar acceleration of the thermal decomposition of a hydrocarbon due to increase in the partial pressure of hydrogen (from 200 to 400 mm Hg) was observed recently in the case of propane [15].

* Thus, for the recombination of isopropyl radicals it is considered that f is about 5×10^{-2} [12], whereas for the recombination of methyl radicals at moderate temperatures f is about unity [13].

In conclusion, let us supplement our analysis by a consideration of the effect of pressure on the values of the rate constants for the reactions examined. It is known that at pressures of up to 2000 - 3000 atm, rate constants of decomposition reactions are slightly reduced. Over the same range of pressures the rate constants of addition and exchange reactions may increase considerably, as is observed, in particular, for esterification, hydrolysis, polymerization, and many other reactions. With rise of pressure, therefore, k_1 and k_3 diminish somewhat, and k_4, k_5, k_6, k_7, and k_8 increase. When there is preferential chain termination at the walls, consideration of the effect of pressure on the rate constants leads to the conclusion that there will be a certain retardation of cracking by increase of pressure, in accordance with equation (4). As regards equations (7) and (10), which appear to characterize the two main types of chain termination during cracking, consideration of them shows that the taking of the effect of pressure on these rate constants into account cannot influence the sign of the pressure effect in these two cases. Thus, the inferences that we have made above concerning the change in the nature of the chain-termination process as the pressure rises still hold good.

SUMMARY

1. An analysis of experimental data on the effect of pressure on the rate of thermal cracking of paraffins leads to the conclusion that rise in pressure in the range 1 - 10 atm. approximately, generally accelerates cracking, whereas in the range 100 - 1000 atm. approximately, it retards it.

2. A scheme, consistent with the observed effects of pressure on the rate of the process, has been given for the mechanism of the thermal cracking of paraffins.

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Received June 16, 1953

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 61. REACTIONS OF POLYESTER MACROMOLECULES

V. V. Korshak and S. V. Vinogradova

Our investigation [1] of the polycondensation of 1,6-hexanediol with sebacic acid showed that only at the beginning of the process does reaction between the original substances occur with formation of low-molecular-weight polyesters (molecular weight up to 900, i.e., up to the trimer). The further polycondensation process, as a result of which the macromolecular polyester is formed, proceeds by interaction of the already formed polyester molecules, which are at first of low molecular weight, and later of high molecular weight. Toward the end of the reaction the interaction between the polyester macromolecules themselves becomes the main feature of the process, and determines the final result.

On the basis of these results it was concluded that the molecules of macromolecular compounds are of fairly high reactivity and can react with one another through their end groups at an appreciable rate. This conclusion refutes the previously widely held idea that macromolecules have negligible reactivity owing to their low mobility and to the high viscosity of the surrounding medium. It will be evident that, in all transformations of macromolecular compounds, it will be necessary to take into account the reactions of the macromolecules among themselves as forming an essential factor in the process. However, since our inferences were made on the basis of an investigation of the kinetics of the process, i.e., indirectly, it is necessary to find more direct and reliable proofs of the correctness of these ideas. With this object in view we have carried out the present investigation, in which we have studied the reaction between polyester macromolecules having different end groups.

The polyesters studied consisted of those synthesized by us from sebacic acid and 1,6-hexanediol and obtained (1) with excess of acid and therefore having carboxyl end groups, and (2) with excess of diol and therefore having hydroxyl end groups. A third polyester was prepared from diethyl sebacate and ethylene glycol, and had ethoxyl end groups. The detailed characteristics of these polyesters are given in Table 1.

TABLE 1
Properties of the Original Polyesters

No.	Starting substances	Molar ratio	Properties of the polyester		
			Spec. viscosity	Mol. wt.	End groups
1	Sebacic acid + 1,6-hexanediol	1.3:1	0.037	1265	Carboxyls
2	Sebacic acid + 1,6-hexanediol	1:1.3	0.045	1533	Hydroxyls
3	Diethyl sebacate + ethylene glycol	1.3:1	0.038	1327	Ethoxyls

The polyesters were purified by reprecipitation from benzene solution by means of petroleum ether. Three mixtures for reaction were then prepared from them: 1 + 3, 1 + 2, and 2 + 3, taken in equal amounts by weight. The mixtures were heated for ten hours at 200° under reduced pressure (2 mm Hg). Samples for test were taken at definite intervals of time. The results are given in Table 2.

TABLE 2
Polycondensation of Polyesters

No.	Duration of heating (hr)	Change in the spec. viscosity of the polyester mixture (0.5%)		
		1 + 2	1 + 3	2 + 3
1	0	0.04	0.04	0.04
2	1	0.07	0.04	0.06
3	2	0.08	0.04	0.08
4	4	0.11	0.04	0.11
5	7	0.13	0.04	0.13
6	10	0.14	0.04	0.13

As will be seen from Table 2, the three polyester mixtures behaved very differently: whereas the 1 + 2 and the 2 + 3 mixtures showed a high increase in the viscosity of their solutions after being heated, the 1 + 3 mixture was completely unaffected. For greater clarity we have represented the viscosity changes graphically (Fig. 1).

Fig. 1 shows that, when the polyester mixtures 1 + 2, and 2 + 3 are heated, there is a smooth rise in viscosity, i.e., a continuous increase in the molecular weight of the product of the reaction of the two polyesters, whereas the 1 + 3 mixture undergoes no change in viscosity, and therefore in molecular weight. This indicates quite definitely

the presence of interaction between the original polyesters in the case of the first two mixtures and the absence of any reaction in the case of the third mixture. We may, therefore, consider that we have fully proved the occurrence of reaction between two polyesters resulting in the growth of the macromolecule and the formation of a polyester of higher molecular weight.

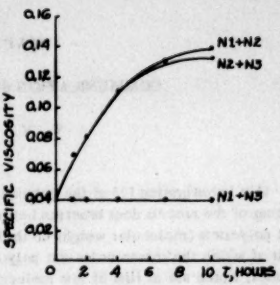

Fig. 1

The difference in the behaviors of the polyester mixtures that we prepared is readily understood when we consider the differences in the nature of the end groups of the polyesters and the effects that they have on the reactivities of the molecules. Polyester No. 1 was prepared with an excess of sebacic acid and all of its end groups are therefore carboxyls. Polyester No. 2 was prepared with an excess of 1,6-hexanediol, and has hydroxyl end groups. A mixture, therefore, of these two polyesters readily reacts by direct esterification between the carboxyl and hydroxyl groups:

$$\begin{aligned}&HOOC(CH_2)_8CO[O(CH_2)_6OOC(CH_2)_8CO]_xOH +\\ &+ H[O(CH_2)_6OOC(CH_2)_8CO]_yO(CH_2)_6OH \longrightarrow H_2O +\\ &+ HOOC(CH_2)_8CO[O(CH_2)_6OOC(CH_2)_8CO]_{x+y}O(CH_2)_6OH.\end{aligned}$$

Polyester No. 3 was prepared from diethyl sebacate and has ethoxyl end groups; it therefore reacts readily with Polyester No. 2, which has hydroxyl end groups. In this case transesterification occurs by alcoholysis, and ethanol is formed in accordance with the equation:

$$C_2H_5OOC(CH_2)_8CO[O(CH_2)_6OOC(CH_2)_8CO]_xOC_2H_5 + H[O(CH_2)_6OOC(CH_2)_8CO]_yO(CH_2)_6OH \longrightarrow$$

$$\longrightarrow C_2H_5OH + C_2H_5OOC(CH_2)_8CO[O(CH_2)_6OOC(CH_2)_8CO]_x-[O(CH_2)_6OOC(CH_2)_8CO]_yO(CH_2)_6OH.$$

As we have shown previously for the polycondensation of bis(2-hydroxyethyl) sebacate [2], the alcoholysis reaction can be used successfully for the synthesis of polyesters. In the present case we have an example of such a reaction in which the alcoholysis occurs not between molecules of the original monomers, but between polyester macromolecules. The smooth course of the alcoholysis reaction in this case proves that there is no difference in principle between the macromolecules and the original monomers with respect to the possibility of the occurrence of a given reaction.

In the case of the mixture of Polymers No. 1 and 3, the picture undergoes a radical change. The end groups of these polyesters are carboxyls and ethoxyls. Interaction between these, either by direct esterification or by alcoholysis, is impossible, as can be readily seen by an examination of the formulas of these polyesters:

$$HOOC(CH_2)_8CO[O(CH_2)_6OOC(CH_2)_8CO]_xOH \quad \text{(Polyester No. 1)}$$

$$C_2H_5OOC(CH_2)_8CO[O(CH_2)_6OOC(CH_2)_8CO]_xOC_2H_5 \quad \text{(Polyester No. 3)}$$

The only possible method of interaction is by acidolysis with separation of sebacic acid or its diethyl ether; but, as we have shown in a previous paper [3], the acidolysis reaction proceeds much less readily than the reactions of alcoholysis and direct esterification. In the present case the occurrence of polycondensation by acidolysis is rendered even less likely by the fact that sebacic acid is considerably less volatile than adipic acid, the esters of which were the subject of our previous investigation. This provides the explanation of the fact that the polyester mixture 1 + 3 does not change when heated, its viscosity in solution and molecular weight, unlike those of the first two mixtures, undergoing no change.

In general, therefore, our results confirm the rule that we have previously noted: in polycondensation the reaction rate and degree of conversion are determined not by the nature of the low-molecular-weight products formed, but by their volatility [3]. If, in fact, we examine the volatilities of the low-molecular weight polycondensation products in the case of our three polyester mixtures, then it will be immediately obvious that there is a correlation between the degree of conversion (in other words, the molecular weight of the polymer) and the volatility of the low-molecular-weight reaction product. In the case of the polyester mixture 1 + 2, the low-molecular-weight reaction product is water, and for the mixture 2 + 3 the corresponding product is ethanol; i.e., both substances are very volatile. Correspondingly, the molecular weight of the polyester rises from 1400 in the original mixture to 4500. In the case of the polyester mixture 1 + 3 the only possible low-molecular-weight products are

sebacic acid and its ester. Both of these substances are of high boiling point and low volatility, and, as a result, there is naturally no rise in molecular weight in this case.

In conclusion we must point out that this investigation of polyesters having carboxyl, hydroxyl, and ethoxyl end groups has confirmed our previous results on the polyesterification reaction and has shown that polyester macromolecules readily react with one another forming compounds of higher molecular weight. A decisive part in this is played by a factor determined by the volatility of the low-molecular-weight product that separates in the given reaction. If a readily volatile product separates, reaction will proceed owing to the rapid displacement of the equilibrium toward the right, but when the low-molecular-weight reaction product is of low volatility, the equilibrium will not be displaced toward the right and no polyesterification will occur.

SUMMARY

1. A study has been made of reactions in three mixtures, each containing two polyesters having different end groups. Three polyester components, having carboxyl, hydroxyl, and ethoxyl end groups respectively, are used.

2. It has been found that the polyester having hydroxyl end groups reacts with the polyesters having carboxyl and ethoxyl end groups.

3. It has been found that the polyester having carboxyl end groups does not react with the polyester having ethoxyl end groups.

4. It has been shown that a decisive factor for the occurrence of polycondensation is the volatility of the low-molecular-weight product that separates; high volatility leads to a displacement of the equilibrium to the right and so to the growth of the polymer molecules.

5. It has been shown that macromolecules have fairly high reactivities, so that they are capable of undergoing the same reactions as the monomers are.

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Received November 5, 1952

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* See Consultants Bureau Translation, page 483.
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BRIEF COMMUNICATIONS

PREPARATION OF TETRAPHENYL- AND TETRA-p-TOLYLY-LEAD BY THE DECOMPOSITION OF ARENEDIAZONIUM FLUOBORATES WITH LEAD – SODIUM ALLOY

A. N. Nesmeyanov and L. G. Makarova

By the decomposition of benzenediazonium fluoborate with lead powder in acetone, one of us, together with Kocheshkov and Nad [1], has prepared tetraphenyllead in 15% yield. It was not found possible to obtain any organolead compound when other arenediazonium fluoborates were decomposed with lead powder. It is now found, however, that if, instead of lead powder, a lead-sodium alloy (containing 10% sodium) is used for the decomposition of arenediazonium fluoborates in acetone, tetraphenyllead is obtained in 30% yield, and tetra-p-tolyllead is obtained in 15% yield.

EXPERIMENTAL

Preparation of Tetraphenyllead. Over a period of 90 minutes 7.5 g of a lead-sodium alloy (10% Na) was introduced into a cooled (ice water) vigorously stirred (Witt stirrer) suspension of 10 g of benzenediazonium fluoborate in 60 ml of dry acetone. Nitrogen was evolved. The initial temperature was +4°, and the maximum temperature was +13°. When the whole of the alloy had been added, the mixture, cooled with ice water, was stirred for four hours. On the next day the acetone was distilled off, and the residue was washed with ether and then treated in an extractor with chloroform. The chloroform was evaporated off, and the residue was washed with ether and crystallized from chloroform. The melting point, and also a mixture melting point with known tetraphenyllead, was 225°. The yield was 2.07 g (30%). The residue in the extraction thimble did not burn when heated with copper oxide.

Preparation of Tetra-p-tolyllead. Over a period of ten minutes 7.2 g of a lead-sodium alloy (10% Na) was introduced into a cooled (by ice water to +6°) stirred suspension of 10.3 g p-toluenediazonium fluoborate in 60 ml of dry acetone. After 1½ minutes evolution of nitrogen began and the temperature rose to +14°. When the addition of alloy was complete, the mixture, cooled with ice water, was stirred for one hour, and was then set aside overnight at room temperature. On the next day the precipitate was filtered off by suction, washed with ether, and treated in an extractor with chloroform. The residue remaining after evaporation of the chloroform was washed with ether and crystallized from a mixture of acetone and chloroform. The yield was 1.11 g (15.6%). After recrystallization from chloroform, it melted at 240° (for the melting point of tetra-p-tolyllead the literature [2] gives 240°). When acetone was evaporated from the filtrate from the original precipitate, there remained a black, viscous mass, which did not contain lead. The residue in the extraction thimble did not contain any organolead compounds (tested with copper oxide).

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Received November 21, 1953

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DIAMAGNETIC SUSCEPTIBILITY OF SOME ORGANIC COMPOUNDS

M. A. Luferova and Ya. K. Syrkin

By a method that has been described previously [1] we have measured the diamagnetic susceptibilities of twenty organic compounds, namely, certain 1- and 2-substituted naphthalenes, some o-, m-, and p-disubstituted benzenes, and some urea derivatives. The values found for the molecular susceptibilities are given in the table.

TABLE

Substance	$-\chi \cdot 10^6$	Substance	$-\chi \cdot 10^6$
1-Naphthol	95.22	o-Nitrophenol	68.97
2-Naphthol	98.25	m-Nitrophenol	65.91
1-Naphthylamine	91.85	p-Dichlorobenzene	81.73
2-Naphthylamine	98.00	1-Chloro-4-iodobenzene	99.42
1-Methylnaphthalene	102.15	p-Iodotoluene	101.31
2-Methylnaphthalene	108.83	Carbanilide	134.05
1-Nitronaphthalene	98.47	$C_6H_5NH \cdot CO \cdot NH \cdot C_6H_5$	
2-Naphthalenesulfonyl chloride	121.91	3-Nitrocarbanilide	148.1
2-Naphthalenesulfonamide	127.60		
o-Nitroaniline	67.64	$C_6H_5NHCONHC_6H_4(NO_2)$	
m-Nitroaniline	59.77	2-Methylcarbanilide	154.0
p-Nitroaniline	63.36	$C_6H_5NHCONH \cdot C_6H_4(CH_3)$	

In all of the investigated cases the diamagnetic susceptibilities (DS) of 2-substituted naphthalenes are greater, than those of the corresponding 1-substituted naphthalenes in absolute magnitude. As is well known, a similar regularity is to be observed also for the dipole moments of 1- and 2-substituted naphthalenes. Pascal's additive values are different from those found experimentally. Thus, for naphthol the additive value of the DS is 96.14, for naphthylamine it is 99.07, for methylnaphthalene it is 103.4, and for nitronaphthalene it is 96.71.

The benzene derivatives were studied in relation to the indications given in the literature that the maximum DS is possessed by ortho derivatives when the groups are ortho-para-orienting, and by the meta derivatives when the groups are meta-orienting [2]. In the case of the nitroanilines, the order of the DS values is as follows:

ortho > para > meta.

For 1-chloro-4-iodobenzene and the last two compounds in the table, the respective additive DS values are 107.27, 135.21 and 141.90. It will be seen that these values differ appreciably from the experimental values. A detailed consideration of the results given in the table, and also of data for other compounds, will form the subject of a further paper.

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Received November 16, 1953

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DIPOLE MOMENTS OF SOME ORGANIC MOLECULES

E. A. Shott-Lvova and Ya. K. Syrkin

By means of the heterodyne method in benzene solution at 25° we have measured the dipole moments of a number of organic compounds, including hydroxy compounds, azonaphthalenes and their derivatives, and also derivatives of adipic acid. Below we give a table in which we indicate the range of concentrations studied (mole fractions), the total polarizations $\underline{P}$, the electron polarizations P_E, and the values of the dipole moments. The dipole moment of 4-cyclohexyloxypyridine differs greatly from the value calculated by vector addition, which indicates the appreciable part played by the oxonium state of the oxygen in this compound. In the case of 4-phenoxypyridine, the effect of the phenyl group is felt: this may displace an electron toward itself and give a component moment at an angle of 110°, which must lead to a diminution in the moment, as compared with the first compound in the table. Unlike these compounds, vinyl ethers have moments close to the value of the moment of the linkage C–O–C in the usual ethers.

A comparison of 1- and 2-substituted naphthalenes shows that the moment of 2,2'-azonaphthalene is greater than that of 1,1'-azonaphthalene. A similar regularity is observed also for a number of other α- and β-derivatives. The dipole moments of the adipic acid derivatives were determined in connection with the question of internal rotation about single bonds. The moments of adiponitrile and diethyl adipate were determined also at 50°; a slight dependence on temperature was observed. A detailed discussion of the results will appear in the future.

TABLE

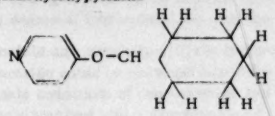
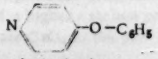
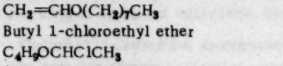
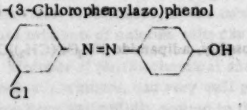
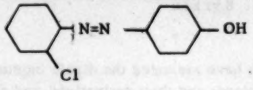
No.	Compound	Concentration (mole fraction)	P	P_E	$\mu \cdot 10^{18}$
1	4-Cyclohexyloxypyridine 	0.074 -0.013	300.9	51.32	3.46
2	4-Phenoxypyridine 	0.01 -0.012	181.2	47.03	2.54
3	Phenyl vinyl ether $CH_2=CH-O-C_6H_5$	0.017 -0.098	62.88	37.53	1.1
4	Octyl vinyl ether $CH_2=CHO(CH_2)_7CH_3$	0.017 -0.044	79.53	49.53	1.2
5	Butyl 1-chloroethyl ether $C_4H_9OCHClCH_3$	0.019 -0.056	125.96	36.42	2.07
6	1,1'-Azonaphthalene	0.012 -0.022	98.27	91.12	0.59
7	2,2'-Azonaphthalene	0.002 -0.0025	114.98	91.12	1.07
8	4-(4-Chlorophenylazo)phenol 	0.0038-0.0046	211.56	55.13	2.74
9	4-(3-Chlorophenylazo)phenol 	0.004 -0.0045	189.2	55.13	2.54

TABLE -- (continued)

No.	Compound	Concentration (mole fraction)	P	P_E	$\mu \cdot 10^{18}$
10	4-(2-Chlorophenylazo)phenol 	0.0021-0.0035	153.98	55.13	2.18
11	Adiponitrile $CN(CH_2)_4CN$	0.0079-0.015	330.93	29.99	3.81
12	Diethyl adipate $C_2H_5OOC(CH_2)_4COOC_2H_5$	0.009 -0.028	173.18	51.69	2.42
13	Putrescine • $NH_2(CH_2)_4NH_2$	0.001 -0.005	148.49	35.31	2.33

Received November 16, 1953

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• The literal translation of the Russian is "the diamine of adipic acid". Possibly, adipamide $NH_2CO(CH_2)_4CONH_2$ is intended. PUBLISHER.

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SYSTEMS CONTAINING CONCENTRATED HYDROGEN PEROXIDE

COMMUNICATION 4. SOLUBILITY ISOTHERMS OF THE TERNARY SYSTEM $Ca(OH)_2-H_2O_2-H_2O$

S. Z. Makarov and N. K. Grigoryeva

There are indications in the literature of the existence of the following calcium peroxy compounds: calcium peroxide octahydrate $CaO_2 \cdot 8H_2O$, calcium peroxide dihydrate $CaO_2 \cdot 2H_2O$, anhydrous calcium peroxide CaO_2, and calcium peroxide diperhydrate, which contains hydrogen peroxide of crystallization and has the formula $CaO_2 \cdot 2H_2O_2$. Attempts have been made to demonstrate the existence of calcium tetroxide CaO_4 as an impurity in CaO_2. However, the material in the literature on this question is very contradictory and gives rise to considerable doubt.

Calcium peroxide was prepared by Thenard [1] in 1818 in the form of $CaO_2 \cdot 8H_2O$ by the reaction of aqueous hydrogen peroxide solutions with lime water. In 1866 Schöne [2], and in 1873 Conroy [3], confirmed this formula; Schöne stated that the crystals of calcium peroxide octahydrate are square in shape. Calcium peroxide formed the subject of some careful investigations by Forcrand [4, 5, 6], who studied heats of reaction for the action of various amounts of hydrogen peroxide on calcium oxide and obtained two compounds: $CaO_2 \cdot 2H_2O$ and $CaO_2 \cdot 8H_2O$. He related the degree of hydration of the calcium peroxide to the ratio of CaO to H_2O_2 and the reaction temperature.

Riesenfeld and Nottebohm [7] showed that, apart from calcium peroxide di- and octa-hydrates, anhydrous calcium peroxide could be obtained directly from calcium salts, aqueous ammonia, and hydrogen peroxide by the use of suitable conditions of concentration and temperature; they showed also that CaO_2 exists in two modifications. These authors prepared also a diperhydrate of calcium peroxide by reaction of concentrated H_2O_2 with $CaO_2 \cdot 8H_2O$ at low temperature. Traube and Schulze [8] made a study of calcium peroxide and postulated the existence of a higher calcium peroxide CaO_4, accompanying CaO_2 as an impurity to the extent of 5-8%, but they did not isolate CaO_4 in the pure state.

Kotov and Raikhshtein [9] and Kazarnovsky [10] studied the X-ray structures of alkali and alkaline-earth peroxides. These peroxides have lattices of the calcium carbide type, elongated in one direction owing to the elongated form of the O_2^{--} ion. The crystals, therefore, belong to the tetragonal, and not the cubical, syngony. The two oxygen atoms are equivalent, being linked by a homopolar bond.

Ehrlich [11] carried out determinations of the magnetic susceptibilities of calcium di- and tetra-oxides in a calcium peroxide sample containing about 5% of CaO_4 and established that CaO_4 contains the O_2^- ion.

Astakhov and Getsov [12], who also studied the structure of calcium tetroxide, concluded that CaO_4 has an ionic lattice formed by Ca^{++} and O_2^- ions.

It must be emphasized that all of the investigations on the peroxy compounds of calcium have been of a purely preparative nature: they cannot answer the question of the exact compositions and natures of the compounds formed, of their fields of existence, of the conditions under which the interaction products formed from hydrogen peroxide and aqueous solutions of calcium salts can be obtained, and of the chemical changes that occur in the system.

Methods of physicochemical analysis, which have been developed by N. S. Kurnakov into an independent branch of physical chemistry, can very well provide the answers to these questions. These methods of physicochemical analysis have been successfully applied to the study of the systems: 1) sodium carbonates and H_2O_2 [13], and 2) urea and H_2O_2 [14]. This method is now applied for the first time to a system in which $Ca(OH)_2$ and H_2O_2 are components.

The binary system $Ca(OH)_2-H_2O$ has been studied by many investigators. Data published in the period 1878-1934 on the solubility of CaO in water have been collected by Seidell [15]. Recent results, obtained by Haslam [16] and Bossett [17], indicate that the solubility of $Ca(OH)_2$ falls as the temperature rises. The solubility of $Ca(OH)_2$ in water falls almost linearly, and the existence of any hydrates is, therefore, excluded.

From 1900 onwards, the binary system $H_2O_2-H_2O$ has been investigated by many chemists. It was at first considered that solid solutions were formed in all of the solid phases of the system. However, the work of Foley and Giguere [18], which appeared in 1951, completely refuted the existence of solid solutions of water in hydrogen peroxide and of hydrogen peroxide in water. Independently, Mironov and Bergman [19] also established the absence of solid solutions in this system.

EXPERIMENTAL

The ternary system $Ca(OH)_2-H_2O_2-H_2O$ was investigated by the solubility method at three temperatures, 0°, −10°, and −21°, under isothermal conditions. The system was studied over a wide range of hydrogen peroxide concentration, the solid phases being investigated by chemical and thermal analysis. In the solutions of this system equilibrium was established by stirring for 1-2 hours, depending on the H_2O_2 content of the liquid phase. At high H_2O_2 concentrations, the establishment of equilibrium was complicated by the decomposition of the hydrogen peroxide, resulting in a corresponding displacement of the equilibrium.

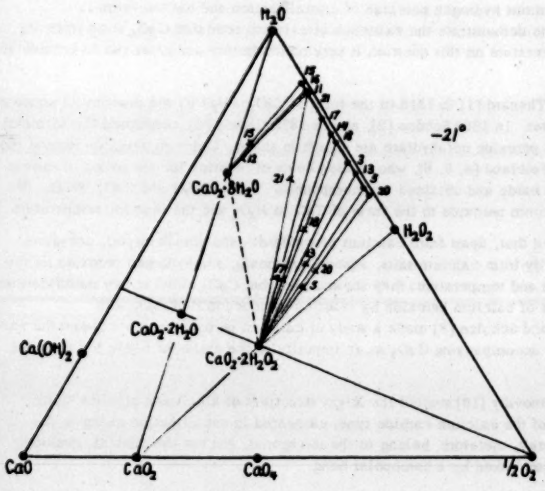

Fig. 1

Substances of high purity were used: $Ca(OH)_2$, containing 76.02% of CaO and 23.98% of H_2O, but no detectable traces of CO_2, and prepared from calcium hydroxide (Glavkhimreaktiv "pure" brand) by calcination at 800-900° followed by slaking with water to $Ca(OH)_2$ with exclusion of carbon dioxide; calcium peroxide octahydrate, containing 7.4% of active oxygen and 26.77% of CaO, and prepared by the ammonia method from $CaCl_2 \cdot 6H_2O$; calcium peroxide containing 20.5% active oxygen; hydrogen peroxide of various concentrations, freed from stabilizer by fractional vacuum distillation.

Test samples of the liquid phases and residues were taken by filtration of the mixture through a Schott No. 2 or No. 3 funnel (under suction), the operation being carried out isothermally at the temperature of the experiment. Both the liquid phase and the residue were analyzed for active oxygen and calcium. Test samples for determination of active oxygen were placed in small beakers for weighing together with borate stabilizers. The samples for the determination of CaO were weighed in beakers without the addition of stabilizers. Active oxygen was determined by titration in presence of sulfuric acid with 0.1 N $KMnO_4$. Calcium, after precipitation as oxalate, was also titrated with 0.1 N $KMnO_4$. The analytical results were calculated as CaO, CaO_2, and H_2O. The results (% by weight) were plotted on the triangular diagram $CaO-CaO_2-H_2O$. The compositions of the solid phases were determined graphically and analytically by the residue method.

Study of the −21° isotherm of this system is confined to H_2O_2 concentrations in the range 26-82%, since, according to Foley and Giguère and also to Mironov and Bergman, hydrogen peroxide solutions containing less than 26% or more than 82% of H_2O_2 are already frozen at −21°. For the −10° isotherm the non-freezing region is extended to 15-91% H_2O_2.

TABLE 1

−21° Isotherm for the System $Ca(OH)_2$−H_2O_2−H_2O

Point No.	Concn. of orig. H_2O_2 (% by wt.) as H_2O_2	Concn. of orig. H_2O_2 (% by wt.) as active O_2	Composition of liquid phase (% by weight) $\frac{1}{2}O_2$	CaO	H_2O	Composition of residue (% by weight) $\frac{1}{2}O_2$	CaO	H_2O	Composition of solid phases	Starting material
12	24.5	11.5	11.5	0.81	87.6	9.1	21.7	69.2	$CaO_2 \cdot 8H_2O$	$Ca(OH)_2$
16	26.0	12.2	11.8	0.83	87.4	9.0	16.5	74.5	The same	$CaO_2 \cdot 8H_2O$
11	28.0	13.2	13.0	0.82	86.0	10.0	17.0	73.0	"	$Ca(OH)_2$
15	30.0	14.1	12.7	0.90	86.4	9.6	17.5	72.9	"	$CaO_2 \cdot 8H_2O$
21	32.6	15.3	14.1	0.13	85.8	20.9	14.7	64.7	$CaO_2 \cdot 2H_2O_2$	$CaO_2 \cdot 8H_2O$
8	44.0	20.7	16.9	0.38	82.7	28.7	32.2	39.1	The same	$Ca(OH)_2$
17	50.0	23.5	19.7	0.40	79.9	30.3	28.6	41.1	"	$CaO_2 \cdot 8H_2O$
2	52.0	24.5	21.2	0.38	78.4	28.9	25.4	45.7	"	$Ca(OH)_2$
6	60.0	28.2	25.6	0.37	74.0	30.5	28.7	40.8	"	$Ca(OH)_2$
14	60.5	28.4	23.2	0.37	76.4	32.8	29.0	38.2	"	$CaO_2 \cdot 8H_2O$
18	60.0	28.2	25.0	0.55	74.4	29.7	18.0	52.3	"	$CaO_2 \cdot 8H_2O$
3	70.0	32.9	30.2	0.33	69.5	32.0	31.9	36.1	"	$Ca(OH)_2$
10	79.0	37.1	34.5	0.28	65.3	33.2	23.4	44.4	"	$Ca(OH)_2$
13	83.0	39.0	33.1	0.33	66.6	33.1	22.0	44.9	"	$Ca(OH)_2$
7	83.6	39.3	36.2	0.21	63.6	34.4	20.2	45.4	"	$Ca(OH)_2$
5	88.0	41.3	35.7	0.18	64.1	34.8	26.0	39.2	"	$Ca(OH)_2$
20	95.6	44.9	38.0	0.23	61.8	35.0	20.8	44.2	"	$CaO_2 \cdot 8H_2O$

TABLE 2

−10° Isotherm for the System $Ca(OH)_2$−H_2O_2−H_2O

Point No.	Concn. of orig. H_2O_2 (% by wt.) as H_2O_2	Concn. of orig. H_2O_2 (% by wt.) as active O_2	Composition of liquid phase (% by weight) $\frac{1}{2}O_2$	CaO	H_2O	Composition of residue (% by weight) $\frac{1}{2}O_2$	CaO	H_2O	Composition of solid phases	Starting material
17	18.0	8.8	7.0	0.25	92.7	7.7	21.7	71.7	$CaO_2 \cdot 8H_2O$	$Ca(OH)_2$
15	25.4	11.9	10.3	0.50	89.2	9.5	17.8	72.6	$CaO_2 \cdot 8H_2O$	The same
23	27.5	12.9	9.9	0.48	89.6	17.4	21.6	61.0	transition points	"
24	27.5	12.9	10.5	0.56	88.9	14.7	18.5	66.8	$CaO_2 \cdot 8H_2O$ +	"
25	27.5	12.9	9.2	0.40	90.4	18.5	19.9	61.6	$CaO_2 \cdot 2H_2O_2$	"
2	30.4	14.3	10.0	0.32	89.7	20.3	18.6	61.2	$CaO_2 \cdot 2H_2O_2$	"
22	39.0	18.3	14.4	0.36	85.2	26.0	23.0	51.0	The same	"
4	46.0	21.6	17.7	0.36	82.0	25.6	22.6	51.8	"	"
26	56.0	26.3	21.2	0.35	78.5	30.5	29.5	40.0	"	"
21	58.0	27.3	24.6	0.36	75.0	30.0	26.3	43.7	"	$CaO_2 \cdot 8H_2O$
5	61.3	28.8	24.3	0.33	75.3	29.4	29.6	41.0	"	$Ca(OH)_2$
8	61.3	28.8	27.0	0.36	72.7	29.6	29.5	40.9	"	CaO_2
20	64.0	30.1	27.2	0.32	72.5	30.6	25.6	43.8	"	$Ca(OH)_2$
19	68.5	32.6	29.2	0.30	70.5	30.9	26.1	42.9	"	The same
16	75.0	35.0	32.5	0.25	67.2	32.8	21.3	45.9	"	"
27	83.0	39.0	35.8	0.23	64.0	34.0	23.5	42.5	"	$CaO_2 \cdot 8H_2O$
6	84.0	39.5	36.3	0.21	63.5	35.2	16.3	48.6	"	$Ca(OH)_2$
9	91.0	42.8	40.6	0.16	59.2	35.7	25.4	39.3	"	CaO_2
28	97.0	45.6	43.5	0.10	56.4	39.0	19.5	41.5	"	$CaO_2 \cdot 8H_2O$
14	97.5	45.8	43.3	0.07	56.6	40.1	17.6	42.3	"	$Ca(OH)_2$

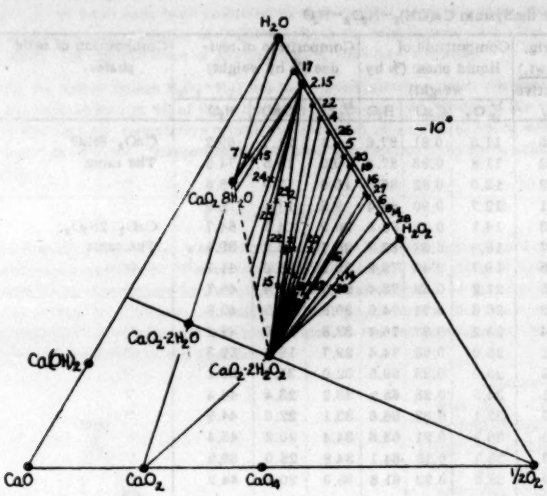
H_2O
$-10°$
$CaO_2 \cdot 8H_2O$
H_2O_2
$CaO_2 \cdot 2H_2O$
$CaO_2 \cdot 2H_2O_2$
$Ca(OH)_2$
CaO
CaO_2
CaO_4
$1/2O_2$

Fig. 2

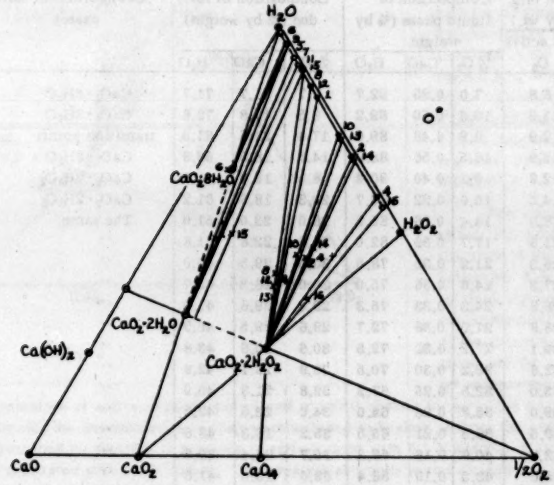
H_2O
0°
$CaO_2 \cdot 8H_2O$
H_2O_2
$CaO_2 \cdot 2H_2O$
$CaO_2 \cdot 2H_2O_2$
$Ca(OH)_2$
CaO
CaO_2
CaO_4
$1/2O_2$

Fig. 3

TABLE 3

0° Isotherm for the System $Ca(OH)_2-H_2O_2-H_2O$

Point No.	Concn. of orig. H_2O_2 (% by wt.) as H_2O_2	Concn. of orig. H_2O_2 (% by wt.) as active O_2	Composition of liquid phase (% by weight) $\frac{1}{2}O_2$	CaO	H_2O	Composition of residue (% by weight) $\frac{1}{2}O_2$	CaO	H_2O	Composition of solid phases	Starting material
6	3.8	1.8	None	0.05	99.95	6.2	27.9	65.8	$CaO_2 \cdot 8H_2O$	$Ca(OH)_2$
9	12.1	5.8	2.25	0.40	97.35	7.8	25.4	66.8	$CaO_2 \cdot 8H_2O$	The same
5	12.8	6.0	3.40	0.10	96.50	11.5	34.6	53.8	$CaO_2 \cdot 2H_2O$	"
7	22.5	10.6	6.60	0.22	93.18	13.8	36.4	49.8	The same	"
11	26.0	12.2	8.05	0.26	91.69	14.1	35.1	50.9	"	"
15	28.0	13.2	9.60	0.32	90.1	14.5	33.3	52.2	"	"
12	31.0	14.6	13.2	0.61	86.19	28.0	30.5	41.5	$CaO_2 \cdot 2H_2O_2$	$CaO_2 \cdot 8H_2O$
8	31.4	14.8	9.3	0.33	90.37	26.7	30.5	42.8	The same	$Ca(OH)_2$
1	44.0	20.7	15.6	0.37	84.03	26.8	27.2	46.0	"	The same
10	60.0	28.2	24.5	0.37	75.13	28.8	23.7	47.5	"	"
13	60.0	28.2	24.9	0.37	74.73	31.2	33.5	35.3	"	$CaO_2 \cdot 8H_2O$
2	70.0	32.9	29.7	0.30	70.0	31.6	21.9	46.5	"	$Ca(OH)_2$
4	88.0	41.3	39.1	0.14	60.76	35.6	18.6	45.8	"	$Ca(OH)_2$
14	96.7	45.4	30.4	0.27	69.33	32.2	19.0	48.8	"	$CaO_2 \cdot 8H_2O$
16	97.0	45.6	41.4	0.14	58.56	36.5	26.3	37.2	"	$CaO_2 \cdot 8H_2O$

The results of the investigation of the ternary system $Ca(OH)_2-H_2O_2-H_2O$ at the three temperatures −21°, −10°, and 0° are given in Tables 1, 2, and 3, and are represented graphically in Figs. 1, 2, and 3. They show successive changes in the compositions of the liquid and equilibrium solid phases as the hydrogen peroxide content of the solutions increases.

The solubility isotherms of the system $Ca(OH)_2-H_2O_2-H_2O$ at −21° and −10° are characterized by two solid phases of composition $CaO_2 \cdot 8H_2O$ and $CaO_2 \cdot 2H_2O_2$. At −21° the field of existence of calcium peroxide octahydrate is very limited, namely, 24.5-28% H_2O_2 in the liquid phase; at −10° it is 14.8-21.9% H_2O_2. A very small increase in the H_2O_2 concentration of the liquid phase results in the immediate formation of calcium peroxide diperhydrate, the addition product formed by H_2O_2 with anhydrous CaO_2. The upper limit of the field of existence of $CaO_2 \cdot 2H_2O_2$ is determined by the temperature at which hydrogen peroxide solutions freeze, namely: at −21° the H_2O_2 concentration reaches 81% and at −10° it reaches 92%.

The 0° solubility isotherm is characterized by the presence of three solid phases of composition:

$CaO_2 \cdot 8H_2O$, existing up to 5-6% H_2O_2 in the liquid phase;
$CaO_2 \cdot 2H_2O$, existing in the range 7-20% H_2O_2;
$CaO_2 \cdot 2H_2O_2$, existing from 20 to 88% H_2O_2.

When the H_2O_2 content of the liquid phase is above 88%, it is very difficult to establish equilibrium in the system owing to vigorous decomposition of hydrogen peroxide and products of its reaction with the solid phases taken.

Calcium peroxide dihydrate $CaO_2 \cdot 2H_2O$ made its first appearance in the study of the 0° isotherm. At lower temperatures no field of existence was observed.

SUMMARY

1. A study of the interaction of aqueous solutions of calcium hydroxide with hydrogen peroxide over a wide range of concentrations, carried out by the solubility method applied to the ternary system

$$Ca(OH)_2-H_2O_2-H_2O$$

at 0°, −10°, and −21°, has made it possible to determine the actual composition and limits of existence of the stable solid phases.

2. The calcium peroxy compounds whose existence is fully established by the study of the ternary system $Ca(OH)_2-H_2O_2-H_2O$ at 0°, −10°, and −21° are: $CaO_2 \cdot 8H_2O$; $CaO_2 \cdot 2H_2O$ and $CaO_2 \cdot 2H_2O_2$.

3. Formation of calcium peroxide octahydrate occurs under restricted conditions at low hydrogen peroxide concentrations.

4. Calcium peroxide diperhydrate is formed over a wide range of hydrogen peroxide concentrations and is relatively stable only at low temperatures.

Received July 2, 1953

Peroxy Compound Laboratory of the USSR Academy of Sciences

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SOLUBILITY OF THE ELEMENTS IN TITANIUM

I. I. Kornilov

Titanium, an element of Group IV of Mendeleev's periodic system of the elements, is generally regarded as a rare element, although in comparison with some other "common" elements it is widely distributed in the earth's crust [1, 2, 3]. Among metals of practical importance, it occupies fourth place with respect to its abundance in the earth's crust; of the 15% total metal content, aluminum accounts for 8.14%, iron 5.12%, magnesium 2.10%, and titanium 0.61%. The content of all of the remaining metals, including such "common" metals as nickel, chromium, copper, and others, is only 0.2%.

Methods have now been developed for the preparation of metallic titanium [1, 2, 3, 4]. It is obtained by the reduction of titanic chloride with molten magnesium by the reaction: $TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$; and also by the thermal dissociation of titanic iodide according to the reaction: $TiI_4 \rightarrow Ti + 2I_2$, and condensation of the metallic titanium on an incandescent molybdenum wire [4, 5]. The second method gives the purest titanium: the so-called "iodide" titanium. Table 1 gives the chemical compositions of titaniums obtained by the two methods.

The principal properties of the titaniums obtained from $TiCl_4$ and from TiI_4 are given in Table 2 [2, 3].

TABLE 1

Chemical Composition of Metallic Titanium

Method of preparation	Ti%	Fe%	Al%	Si%	Mg%
From titanic chloride	99.1	0.06-0.09	–	0.005-0.01	0.03-0.05
From titanic iodide	99.9	0.01-0.05	0.05-0.1	0.01-0.05	0.005

Method of preparation	Mo%	Ca%	C%	N%	O%	H%
From titanic chloride	–	–	0.01-0.04	0.006-0.03	–	0.09-0.20
From titanic iodide	0.05-0.1	0.01-0.05	0.02-0.03	0.002-0.009	–	–

TABLE 2

Properties of Titanium Prepared by Different Methods

Property	from $TiCl_4$	from TiI_4
Melting point (°C)	1725	1725
Type of crystal lattice		
α-modification	Hexagonal	
β-modification	Body-centered	
Temperature of polymorphous transition (°C)	882	885
Specific gravity (g/cc)	4.5	4.5
Resistivity (X 10^{-4} ohm.cm)	0.475	0.475
Coefficient of linear expansion at 20°		$8.5 \cdot 10^{-6}$
Breaking strength (kg/sq.mm)	49-56	27-34
Extension at break (%)	25-30	40
Brinell hardness (kg/sq.mm)	220	100-160

The properties of titanium, like those of other metals, are greatly affected by alloying with other metals, or, in certain cases, metalloids. Titanium is able to form solid solutions and compounds having bonds of a metallic character with many metals. The general laws for the formation of metallic solid solutions and compounds [6, 7], which have been derived by application of Mendeleev's periodic law of the elements, are equally applicable to a study of the interaction of titanium with other elements of the periodic system.

TABLE 3

Dependence of the Solubility of the Elements in Titanium on the Difference in Atomic Diameters (arranged by Groups)

Group	Element	Atomic diameter	Difference (%)	Solubility according to literature (with reference), or expected solubility (no reference)
1	2	3	4	5
				Subgroup A
1	H	1.20	–	Solid interstitial solutions and titanium hydride TiH_2 [10]
1	Li	3.13	6.8	
1	Na	3.83	30.7	Insoluble
1	K	4.76	62.4	"
1	Rb	5.40	84.3	"
1	Cs	5.40	84.3	"
2	Be	2.25	23.2	Very limited solubility [2]
2	Mg	3.20	9.5	Insoluble
2	Ca	3.93	34.1	"
2	Sr	4.29	46	"
2	Ba	4.48	52.9	"
2	Ra	–	–	"
3	B	1.94	34.3	Very limited solid solutions [11]
3	Al	2.80	4.4	Large field of solid solutions [12]. Break in solubility due to difference in crystal lattice
3	Sc	3.02	3.0	Continuous solubility
3	Y	3.62	23.5	Very limited solubility
3	Ti	2.93	–	Continuous solubility
4	Zr	3.19	8.8	Continuous solubility of the two modifications α and β [14]
4	Hf	3.17	8.2	Continuous solubility of the two modifications α and β
4	Th	3.60	23.2	Very limited solubility
5	V	2.69	8.2	Continuous solubility in β-Ti [16]
5	Nb	2.94	0.4	The same in β-Ti [17]
5	Ta	2.94	0.4	" in β-Ti [18]
6	Cr	2.57	12.3	" in β-Ti [19]
6	Mo	2.80	4.4	" in β-Ti [20]
6	W	2.82	4.0	Considerable field of solid solutions in β-Ti [18]
6	U	2.81	4.1	Break in solubility due to difference in crystal lattice
7	Mn	2.60	11.25	Limited solubility in α- and β-Ti [21]
7	Re	2.75	6.1	Continuous solubility in α-Ti
8	Fe	2.54	13.3	Limited solubility in α- and β-Ti [22]
8	Co	2.50	14.7	Limited solubility in α- and β-Ti [23]
8	Ni	2.49	15.0	Limited solubility in α- and β-Ti [24]
8	Ru	2.67	8.9	The same
8	Rh	2.68	8.5	"
8	Pd	2.75	6.1	Break in solubility due to difference in crystal lattice
8	Os	2.70	7.9	The same
8	Ir	2.71	7.1	"
8	Pt	2.88	1.6	"
				Subgroup B
1	Cu	2.55	12.9	Limited solubility in α- and β-Ti [25]
1	Ag	2.883	1.6	Limited solubility in α- and β-Ti [25]
1	Au	2.877	1.81	Limited solubility in α- and β-Ti
2	Zn	2.748	6.2	
2	Cd	3.042	3.82	Insoluble
2	Hg	3.10	5.8	
3	Ga	2.74	6.5	
3	In	3.138	17.1	Insoluble
3	Tl	3.427	16.9	
4	C	1.54	47.5	Very limited solubility in α- and β-Ti [27, 28]

TABLE 3 (continued)

1	2	3	4	5
4	Si	2,34	20,1	Limited solubility in α- and β-Ti [29]
4	Ge	2,78	5,1	Limited solubility in α- and β-Ti
4	Sn	3,168	8,15	Limited solubility in α- and β-Ti [30]
4	Pb	3,494	19,2	Insoluble [30]
5	N	1,42	51,5	Very limited solubility in α- and β-Ti [32, 33]
5	P	2,20	25,0	Very limited solubility in α- and β-Ti
5	As	2,80	4,45	Limited solubility in α- and β-Ti
5	Sb	3,228	10,2	Limited solubility in α- and β-Ti [30]
5	Bi	3,640	24,2	Insoluble
6	O	1,32	55,0	Limited solubility in α- and β-Ti [36, 37, 38]

As already shown in the case of the solubility of elements in iron, nickel, and chromium [8, 9], the following conditions are favorable for the formation of solid solutions in these metals:

1. similarity in the chemical properties of the metals, which is determined by their positions in the periodic system;

2. a small difference in interatomic distances, not exceeding 8-10% for the formation of continuous solid solutions and 14-16% for the formation of limited solid solutions;

3. isomorphism of crystal structure (for the formation of continuous solid solutions).

When these conditions are observed, the tendency for metals to form solid solutions with one another is at its greatest. These same conditions are applicable to the examination of the question of the solubility of the elements in titanium.

Let us examine the solubility of the elements in titanium according to the groups of Mendeleev's system.

Table 3 includes the elements of the A and B subgroups, listed separately, the elements that interact with titanium to form only compounds of an ionic nature, (halogens, sulfur and its analogs, etc.) and do not form solid solutions or compounds having a bond of metallic character not being included.

1. Solubility in Titanium of Elements of the A Subgroups

Among elements of Group I, only hydrogen at low concentrations forms limited solid solutions of the interstitial type. At high hydrogen concentrations, a titanium hydride of the type TiH_2 is formed in titanium [10]. Apart from lithium, the remaining Group I metals, the alkali metals, differ too much from titanium in atomic diameter, and, therefore, should not form solid solutions with it.

Lithium does not differ greatly in atomic diameter (6,8%). At high temperatures, owing to the great difference between titanium and lithium in coefficient of expansion, this difference will increase to such an extent that it will become unfavorable to the replacement of titanium in the crystal lattice by lithium. These circumstances will prevent the formation of an extensive field of solid solutions of lithium in titanium.

Group II metals, apart from magensium, have atomic diameters that bear unfavorable ratios to the atomic diameter of titanium. With the exception of beryllium, they should not form solid solutions with titanium. The behavior of magnesium is analogous to that of lithium. As experiment shows, magnesium does not react with titanium and does not form solid solutions with it. For this reason, magnesium is used in the technical preparation of titanium from its compounds [1, 2, 3]; the residual magnesium impurity in the titanium is readily driven off by heat in a high vacuum, since it is present in a form that is not chemically bound to the titanium.

With regard to elements of Group III, it must be pointed out that boron, which has a small atomic diameter, can yield very dilute solid solutions. According to the literature [11], its solubility in the α- and β-modifications of titanium does not exceed 0,4%. When the boron content is high, titanium boride TiB is formed.

With aluminum, which is close to titanium in the table and does not differ greatly in atomic diameter, titanium forms solid solutions of considerable concentration. According to the literature [12], the solubility of aluminum in the β-modification of titanium is 34,5%, and in the α-modification 24,5%. Also, transformation of the β solid solution to the α solution occurs by a peritectoid reaction.

There is no information concerning the solubilities of scandium and yttrium in titanium. It may be supposed that scandium will give continuous solid solutions, since it has an isomorphous hexagonal lattice, and that very limited solid solutions will be formed with yttrium.

The Group IV elements zirconium and hafnium are analogs of titanium. All three metals have two modifications α and β, and they have isomorphous structures and close atomic diameters. All these circumstances favor the formation of continuous solid solutions in these systems; they will be continuous for both modifications. It will be clear, therefore, that the systems Tiβ – Zrβ, Tiβ – Hfβ, Zrβ – Hfβ (with body-centered lattice) and Tiα – Zrα, Tiα – Hfα, Zrα – Hfα (with hexagonal lattice) will have phase diagrams corresponding to the continuous solid solutions formed by the two modifications of these metals.

This type of phase diagram can be represented for titanium in the form shown in Fig. 1. In a previous paper [13] we advanced a hypothesis that has found confirmation in subsequent papers concerning the systems titanium–zirconium [14] and zirconium–hafnium [15]. Both of these systems, in both modifications, form continuous solid solutions. There are no data concerning the solubility of thorium in titanium. From the difference (23.2%) in atomic diameter, it may be supposed that the solubility in titanium will be very limited.

The Group V elements vanadium, niobium, and tantalum, which are close to titanium in the table, are close in atomic diameter and are isomorphous with the β-modification of titanium; they should give continuous solid solutions with this modification. The data in the literature are in accord with this supposition: in the systems titanium–vanadium [16], titanium–niobium [17], and titanium–tantalum [18], continuous solid solutions are in fact formed with the β-modification of titanium. These elements lower the temperature of the β ⇌ α polymorphous change of titanium to room temperature. The phase diagram for these titanium systems is similar to that for the system Fe–Ni and is given in Fig. 2.

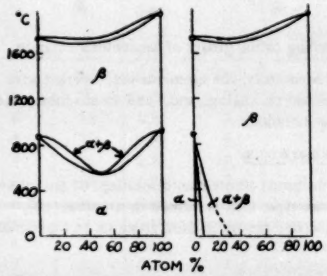

Fig. 1. Phase diagram of the system Ti–Cr.

Fig. 2. Phase diagram of the system Ti–V.

The group of analogs, chromium, molybdenum, and tungsten (Group VI elements), also have favorable atomic diameters and structures isomorphous with the β-modification of titanium. All three metals may give solid solutions with β-titanium. Chromium, which is less favorable with respect to atomic diameter, forms continuous solid solutions with β-Ti and very limited solid solutions showing a eutectoid transformation with α-Ti [19].

The data in the literature on the system titanium–molybdenum [20] show that molybdenum lowers the temperature of the α ⇌ β polymorphous transformation of titanium to room temperature and gives a phase diagram similar to that of Fig. 2. According to the literature [18], the solubility of tungsten in β-Ti is about 50% by weight; its solubility in α-Ti is negligible. In the titanium–tungsten system eutectoid transformation occurs at 715°. Solid solutions should be formed also between titanium and uranium, but there are no data in the literature on this system.

Of elements of Group VII, there is information in the literature only for manganese [21]. Manganese has an appreciable solubility in the β-modification of titanium and negligible solubility in α-Ti. There is no information in the literature concerning the solubility of rhenium in titanium; the favorable relation between the atomic diameters of these two metals and the isomorphism of the structures of rhenium and α-Ti will encourage the formation of solid solutions in this system.

Elements of Group VIII, iron and its analogs, are related less favorable to titanium with respect to atomic diameter than the metals of Groups IV, V, and VI (Table 3). This explains the fact that iron and its analogs (nickel and cobalt) form only limited solid solutions with titanium, both in the β- and also in the α-modification. The solubilities of these three metals are higher in β-Ti than in α-Ti. The transformation β ⇌ α in the systems Ti–Fe [22], Ti–Ni [23], and Ti–Co [24] has a eutectoid character and in this respect are reminiscent of the system Fe–C. Fig. 3 shows a typical phase diagram for such titanium systems having a eutectoid transformation.

As regards the remaining elements of Group VIII, palladium, platinum, and their analogs, there is no information in the literature about their solubilities in titanium. According to the relation of their atomic diameters to that of titanium (Table 3) they should have appreciable solubilities in titanium. Continuity of solid solutions in these systems will be absent owing to the difference between the crystal structure of titanium and those of metals of the palladium and platinum groups.

2. Solubility in Titanium of Elements of the B Subgroups

Passing to an examination of the solubility of elements of the B subgroups in titanium, we must point out that, as in the case of the solubility of elements of the B subgroups in iron, nickel, and chromium (elements of the A subgroups [7, 8, 9] the solubility of these elements in titanium is not completely determined by the conditions given above for the formation of solid solutions of metals. They are not sufficient in all cases to explain the formation, or lack of formation, of solid solutions with titanium. It is probable that significance must be attached here to the difference in electronic structure between the atoms of the elements of these subgroups and titanium atoms and to the different nature of the interaction between valency electrons in such systems. Hence, the most characteristic feature of the interaction of titanium with these elements is the formation of metallic compounds, and not of solid solutions in appreciable concentration.

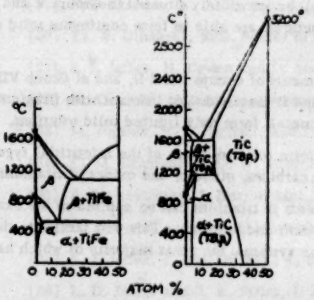

Fig. 3. Phase diagram of the system Ti–Fe.

Fig. 4. Phase diagram of the system Ti–C.

It is probable that even in these cases elements of a given Group will preserve their analogous characters in their interactions with titanium. For example, the information available in the literature shows [25] that titanium forms limited solid solutions with copper that show eutectoid transformation and give a phase diagram reminiscent of that given in Fig. 3.

In the system titanium–copper the compounds Ti_2Cu, TiCu, Ti_2Cu_3, and $TiCu_4$ are formed. There is no information in the literature about the interaction of titanium with the copper analogs silver and gold. It may be supposed that they will behave similarly to copper and also give limited solid solutions and form compounds with titanium.

As regards the Group II metals zinc, cadmium, and mercury, these, being low-melting metals of low boiling point, will not give solid solutions at appreciable concentrations with titanium, even when the atomic diameters are favorable. The same can be said about the following group (Group III) of low-melting metals: gallium, indium, and thalium. They also will proabably not give appreciable ranges of solid solutions with titanium.

Among the elements of Group IV, carbon is of low atomic diameter. This will permit the formation of limited solid solutions of the interstitial type, and also of metallic compounds.

According to the information in the literature [26, 27, 28], carbon forms very limited solid solutions with the α- and β-modifications of titanium, and also a titanium carbide (TiC) of variable composition. The solubility of carbon in β-Ti is less than 0.25% by weight, and in α-Ti it apparently becomes less than 0.1% by weight.

The transformation of these modifications in the titanium–carbon system is effected by peritectoid reaction. The phase diagram of the Ti–C system has the form shown in Fig. 4 [28]. This shows the peritectic transformation and the variable composition of the titanium carbide compound of melting point 3200°. The type of phase diagram shown in Fig. 4 is found also in the system titanium–nitrogen.

The system titanium–silicon [29] is characterized by the formation of limited solid solutions with β- and α-titanium and by eutectic transformation. The solubility of silicon in β-Ti at the eutectic temperature is 3%, and in α-Ti, 0.3%. In this system, the compounds Ti_5Si_3, TiSi, and $TiSi_2$ have been established. The phase diagram of this system is reminiscent of Fig. 3.

There are no data in the literature about the interaction of titanium with the silicon analog germanium. There is some information about the systems titanium–tin and titanium–lead [30, 31, 32]; these metals form solid solutions of low concentration with titanium [30].

Concerning the Group V element nitrogen, there are indications [27, 33, 34] of its limited solubility in α- and β-titanium (about 0.75%), the peritectoid character of the transformations, and the formation of the difficultly soluble compound titanium nitride (TiN). The phase diagram of this system will be similar to that given in Fig. 4. There is no information in the literature about the interaction of titanium with phosphorus, arsenic, and bismuth. It is possible that these elements are able to form metallic compounds with titanium, without an appreciable range of solid solutions. The available information on the system titanium–antimony does not give direct answers concerning the formation of solid solutions of antimony in titanium.

The solubility of oxygen in titanium is also very limited (not more than 0.75% by weight) [36, 37, 38]. The phase diagram of this system near to the titanium axis is similar to the diagram in Fig. 4.

As regards the interaction of titanium with sulfur and its analogs, and with the halogens: as stated above, solid solutions probably do not occur in these systems, only compounds of an ionic nature being formed.

SUMMARY

1. The solubility of the elements in titanium follows a pattern similar to that characterizing the solubility of the elements in other metals, such as iron, nickel, and chromium.

2. The formation, or non-formation, of solid solutions in binary titanium systems is associated with the relative similarity, or dissimilarity, in the properties of the elements, as indicated by Mendeleev's periodic system.

3. Metals which are titanium analogs (zirconium and hafnium), or are closely situated in Groups V and VI, and which differ little in atomic diameter and have isomorphous structures, are able to form continuous solid solutions with titanium.

4. The metals that are the most removed from titanium —elements of Groups I and II, and of Group VIII— have a lower tendency to form solid solutions. Most of the Group I and II metals do not interact with titanium in the liquid or solid state, and do not form solid solutions. Group VIII metals form only limited solid solutions.

5. Elements of low atomic diameter (H, C, N, O) are able to form solid solutions of the interstitial type in low concentration, and to form also interstitial compounds: hydrides, carbides, nitrides, and oxides of titanium.

6. The regularities established for the solubilities of the elements in titanium can be applied to the examination of the solubilities of the elements in the titanium analogs zirconium and hafnium. This will facilitate the general consideration of the phase diagrams of zirconium and hafnium systems, the great majority of which have not been studied.

Received July 9, 1953

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HETEROGENEOUS EQUILIBRIA IN SYSTEMS CONTAINING LITHIUM CHLORIDE AND CHLORIDES OF GROUP II METALS

V. P. Blidin

It is known that lithium chloride interacts with many chlorides of bivalent metals, forming hydrated double salts of various types. Voskresenskaya and Yanatyeva [1], in a study of the system $LiCl-MgCl_2-H_2O$ obtained a salt of composition $LiCl \cdot MgCl_2 \cdot 7H_2O$. Basset and Sandersen [2], in a study of the system $SiCl-CoCl_2-H_2O$ found various double salts, $LiCl \cdot CoCl_2 \cdot 2H_2O$, $7LiCl \cdot 2CoCl_2 \cdot 18H_2O$, $3LiCl \cdot 2CoCl_2 \cdot 6H_2O$, and over a certain concentration range they found solid solutions. Benrahr's[3]investigations established that double LiCl salts of a similar type are formed with nickel and manganese chlorides. On the other hand, in an investigation of the system $LiCl-BeCl_2-H_2O$ Novoselova and Sosnovskaya [4] established that no hydrated double salts were found in this system.

EXPERIMENTAL

As starting materials, salts having the "chemically pure" label were taken and recrystallized twice. Chlorine, according to the acidity of the medium, was determined either gravimetrically, or by Mohr titration with $AgNO_3$ solution. Beryllium was precipitated as hydroxide with dilute ammonia solution, and the hydroxide was dried off in a platinum crucible over a bunsen within the range 1000-1100°. Calcium was precipitated as CaC_2O_4, converted into $CaCl_2$, and determined by titration of the last compound with $AgNO_3$. Barium and strontium were determined gravimetrically. Zinc and cadmium were determined "trilonometrically" with the aid of Trilon B [5]. Mercury was determined volumetrically by the method described by Korenman [6]. In all cases lithium was determined by difference from the total amount of chlorides. The solubilities in the systems were studied in an electrically heated water thermostat, the temperature being maintained constant within $\pm 0.1°$ and controlled with a toluene thermoregulator. The solubilities of the salts were determined in a reaction vessel having a petroleum jelly seal. The solution in the vessel was stirred at constant temperature until equilibrium between the liquid and solid phases was attained, which required from ten hours to three days. The compositions of the solid phases were established by the Schreinemakers "residue" method. In the graphical representation of the equilibria on diagrams we expressed concentrations in percent by weight. The cosolubilities of the components were studied isothermally at 25° and 40°, with the exception of the system $LiCl-HgCl_2-H_2O$, which was studied at 30°.

The 25° and 40° isotherms of the system $LiCl-BeCl_2-H_2O$ (Table 1, Fig. 1). In the investigation of this system, it was found that when $BeCl_2$ was added, the viscosity of the solution increased and settling in the liquid phase lasted a long time. With increase in the LiCl concentration the viscosity diminished, and settling in the liquid phase then occupied only a short period of time.

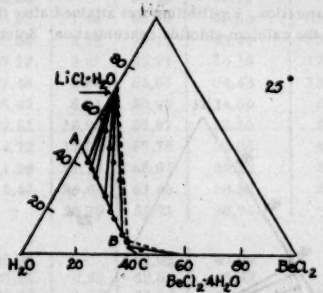

Fig. 1

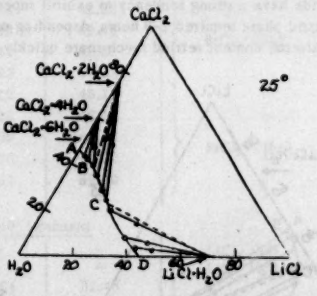

Fig. 2

TABLE 1

Amount (% by weight)			Total amt. of salts (% by weight)	Composition of solid phase (% by weight)		Solid phases
LiCl	$BeCl_2$	H_2O		LiCl	$BeCl_2$	
			25° Isotherm			
45.95	–	54.05	45.95	–	–	
39.46	5.48	55.06	44.94	58.12	2.36	
37.07	7.92	55.01	44.99	56.60	3.17	
33.34	11.52	55.14	44.86	51.75	6.12	
25.27	18.66	56.13	43.87	45.94	10.08	$LiCl \cdot H_2O$
18.67	24.46	56.87	43.13	38.86	14.51	
15.63	27.41	56.96	43.04	36.43	18.20	
9.14	33.25	57.61	42.39	31.51	21.23	
6.20	36.07	57.73	42.27	–	–	$LiCl \cdot H_2O + BeCl_2 \cdot 4H_2O$
2.18	39.65	58.17	41.83	1.62	44.26	$BeCl_2 \cdot 4H_2O$
–	41.72	58.28	41.72	–	–	
			40° Isotherm			
48.98	–	52.02	47.98	–	–	
40.86	6.48	52.66	47.34	58.92	2.51	
37.67	9.56	52.76	47.24	56.80	4.02	
30.75	16.12	53.13	46.87	51.16	8.49	$LiCl \cdot H_2O$
23.52	22.23	54.25	45.75	44.42	12.60	
15.53	30.14	54.33	45.67	39.51	17.47	
7.34	38.02	54.63	45.37	34.10	22.46	$LiCl \cdot H_2O$
5.22	39.86	54.92	45.08	23.55	29.88	
2.14	42.91	54.95	45.05	–	–	$LiCl \cdot H_2O + BeCl_2 \cdot 4H_2O$
–	44.12	55.88	44.12	–	–	$BeCl_2 \cdot 4H_2O$

When the results of Novoselova and Sosnovskaya [4] on the isotherm of the system at 0° are compared with ours, it will be seen that with rise in temperature, the curve (BC) for the crystallization of beryllium chloride is shortened and the curve (AB) for the crystallization of lithium chloride is correspondingly lengthened. Hence, the salting-out power of $BeCl_2$ with respect to LiCl increases with rise in temperature. Although lithium chloride in the systems $LiCl-NaCl-H_2O$ and $LiCl-KCl-H_2O$, studied by us [7], has the role of a salting-out agent, it has no such significance in the present system. It should be pointed out that in the present system, no chemical compounds are formed, whereas the results of Schmidt [8] show that in the system $LiCl-BeCl_2$, in absence of solvent, a compound $2LiCl \cdot BeCl_2$ is formed which melts with decomposition.

The 25° and 40° isotherms of the system $LiCl-CaCl_2-H_2O$ (Table 2, Fig. 2). The formation of viscous solutions in this system made the taking of test samples and the attainment of equilibrium difficult. Aqueous solutions of calcium chloride have a strong tendency to exhibit supersaturation. Equilibrium was attained after three days; settling in the liquid phase required 1-3 hours, depending on the calcium chloride concentration. Solutions of appreciable lithium chloride content settled much more quickly.

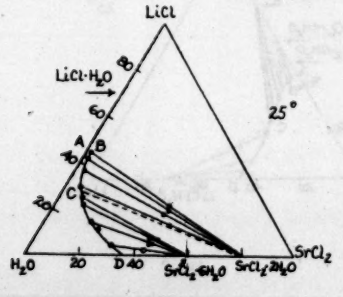

Fig. 3

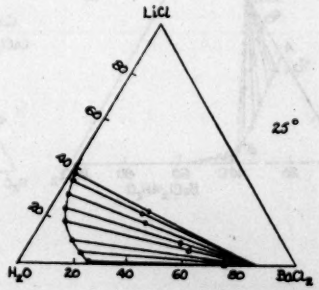

Fig. 4.

TABLE 2

Amount (% by weight) LiCl	$CaCl_2$	H_2O	Total amt. of salts (% by weight)	Composition of solid phase (% by weight) LiCl	$CaCl_2$	Solid phase
			25° Isotherm			
45.98	–	54.02	45.98	–	–	
42.47	30.8	54.45	45.55	48.53	2.46	$LiCl \cdot H_2O$
36.66	8.02	55.32	44.68	45.44	5.21	
24.64	19.48	55.88	44.12	37.31	14.12	
20.51	24.72	54.77	45.23	11.02	48.15	
17.22	28.31	54.47	45.53	8.96	51.64	$CaCl_2 \cdot 2H_2O$
12.13	34.97	52.90	47.10	7.68	50.31	
8.30	39.23	52.47	47.53	5.51	47.23	
5.45	41.62	52.93	47.07	3.44	49.54	$CaCl_2 \cdot 4H_2O$
3.78	42.54	53.68	46.32	2.46	52.62	
–	46.15	53.85	46.15	–	–	$CaCl_2 \cdot 6H_2O$
			40° Isotherm			
47.98	–	52.02	47.98	–	–	
44.01	6.13	49.56	50.14	55.46	3.50	
39.08	12.12	48.80	51.20	52.59	7.03	$LiCl \cdot H_2O$
34.12	20.30	45.58	54.42	48.12	12.47	
29.46	27.58	42.96	57.04	43.80	18.81	
28.05	29.54	42.41	57.59	–	–	$CaCl_2 \cdot 2H_2O + LiCl \cdot H_2O$
26.63	30.82	42.55	57.45	17.24	46.58	
23.87	32.35	43.78	56.22	15.31	47.56	
17.48	38.06	44.46	55.54	13.17	47.94	$CaCl_2 \cdot 2H_2O$
13.27	42.18	44.55	55.45	9.96	49.50	
5.41	50.19	44.40	55.60	5.04	52.76	
2.54	53.10	44.36	55.64	–	–	$CaCl_2 \cdot 4H_2O + CaCl_2 \cdot 2H_2O$
1.67	54.20	44.13	55.87	1.48	55.31	$CaCl_2 \cdot 4H_2O$
–	55.84	44.16	55.84	–	–	

TABLE 3

Point No.	Amount (% by weight) LiCl	$SrCl_2$	H_2O	Total amt. of salts (% by weight)	Composition of solid phase (% by weight) LiCl	$SrCl_2$	Solid phase
				25° Isotherm			
1	45.95	–	54.05	45.95	–	–	$LiCl \cdot H_2O$
2	44.82	1.48	53.70	46.30	21.74	42.62	
3	41.54	2.36	56.10	43.90	19.88	43.86	
4	37.12	3.07	59.81	40.19	17.47	42.51	$SrCl_2 \cdot 2H_2O$
5	29.48	4.95	65.57	34.43	13.23	47.02	
6	25.49	8.51	66.00	34.00	8.12	45.13	
7	22.51	10.62	66.87	33.13	7.98	42.18	
8	14.72	17.53	67.75	32.25	4.09	44.46	
9	11.89	21.14	66.97	33.03	3.50	44.37	$SrCl_2 \cdot 6H_2O$
10	5.48	28.03	66.49	33.51	2.61	42.50	
11	–	36.79	63.21	36.79	–	–	
				40° Isotherm			
1	47.98	–	52.02	47.98	–	–	$LiCl \cdot H_2O$
2	47.01	0.98	52.01	47.99	–	–	$LiCl \cdot H_2O + SrCl_2 \cdot 2H_2O$
3	46.22	1.65	52.13	47.87	29.04	31.48	
4	38.67	3.26	58.07	41.93	22.54	34.70	$SrCl_2 \cdot 2H_2O$
5	31.73	5.84	62.43	37.57	17.25	37.82	
6	25.14	9.98	64.88	35.12	14.48	39.20	
7	17.80	19.25	62.95	37.05	6.60	44.06	$SrCl_2 \cdot 2H_2O + SrCl_2 \cdot 6H_2O$
8	11.66	25.73	62.61	37.39	4.97	45.10	
9	6.05	32.12	61.83	38.17	2.61	47.54	$SrCl_2 \cdot 6H_2O$
10	2.40	36.37	61.23	38.77	1.23	48.69	
11	–	40.12	59.88	40.12	–	–	

On Fig. 2, there are three curves: AB, the crystallization curve of $CaCl_2 \cdot 4H_2O$; BC, the crystallization curve of $CaCl_2 \cdot 2H_2O$ and CD, the lithium chloride monohydrate curve. In spite of some precise work, the curve for $CaCl_2 \cdot 6H_2O$ remained undertermined. These isotherms show quite clearly that in this system, LiCl plays the part of a dehydrating agent. For this and other systems the analytical results for the 40° isotherm were not plotted on the diagram, since they were completely analogous with respect to the crystallization of the respective components to the results for the 25° isotherm.

The 25° and 40° isotherms of the system $LiCl-SiCl_2-H_2O$ (Table 3, Fig. 3). Chemically, calcium chloride is similar to strontium chloride. The latter is offlower solubility and has fewer hydrates than $CaCl_2$. In particular $SrCl_2 \cdot 4H_2O$, is not known. The solutions were not of high viscosity and did not show supersaturation, and settling in the liquid phase required only short periods of time. On Fig. 3 there are three curves: AB, the very short curve for the crystallization $LiCl \cdot H_2O$; BC, the crystallization curve of $SrCl_2 \cdot 2H_2O$ and CD, the $SrCl_2 \cdot 6H_2O$ curve. In this system, lithium chloride dehydrates strontium chloride hexahydrate, which loses four molecules of water and is converted into the dihydrate; at the same time LiCl acts as a salting-out agent.

The 25° isotherm of the system $LiCl-BaCl_2-H_2O$ (Table 4, Fig. 4). This system was studied only at 25°, for at elevated temperatures lithium chloride is precipitated at moderate concentrations.

As will be seen from Fig. 4, in this system, we have only the crystallization curve of barium chloride. This is a feature of those systems in which one of the components acts as a powerful salting-out agent with respect to the other in various solvents. It was not found possible to determine the lithium chloride curve.

TABLE 4

Amount (% by weight)			Total amt. of salts (% by weight)	Composition of solid phase (% by weight)		Solid phases
LiCl	$BaCl_2$	H_2O		LiCl	$BaCl_2$	
			25° Isotherm			
45.95	–	54.05	45.95	–	–	$LiCl \cdot H_2O$
34.12	1.52	64.36	35.64	21.23	33.82	
28.91	3.02	68.07	31.93	17.64	36.48	
23.34	5.54	71.12	28.88	9.15	53.47	
17.48	8.28	74.24	25.76	6.04	58.54	
10.15	14.32	75.53	24.47	3.48	64.92	$BaCl_2 \cdot 2H_2O$
5.16	20.13	74.71	25.29	1.03	71.06	
1.52	24.56	73.92	26.08	0.28	72.37	
–	26.75	73.25	26.75	–	–	

The 25° and 40° isotherms of the system $LiCl-ZnCl_2-H_2O$ (Table 5, Fig. 5). In this system, the establishment of equilibrium required a long time (3-4 days), and in the field of crystallization of zinc chloride the solid phase was a sirupy viscous mass.

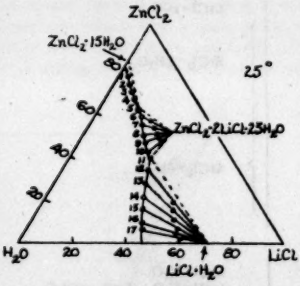

Fig. 5

It will be seen from Fig. 5 that the solubility isotherm for lithium and zinc chlorides consists of three curves: the first curve, from points 1-5, corresponds to the crystallization of $ZnCl_2 \cdot 1.5H_2O$. The composition of the solid phase for this curve coincided with that of the liquid phase, and the point for the composition of the solid phase was, therefore, not plotted. The principal solid phase points were recorded with the aid of a microscope. At point 5, at the limit for the formation of the chemical compound, complete solidification of the system was observed, similar to that observed at the eutectic points of systems at low temperature. At this point, the liquid phase was converted into a continuous gellike mass. Then, after addition of a small amount of saturated LiCl solution, separation of liquid and solid phases was observed. The second curve (points 6-10) corresponds to the compound $ZnCl_2 \cdot 2LiCl \cdot 2.5H_2O$. The tie-lines joining the points (6-10) for the solutions with those for the corresponding "dry" residues meet at the point for the true solid phase, which corresponds to the double salt indicated above. The solubility curve from point 11 to point 17 corresponds to the separation of lithium chloride monohydrate into the solid phase. The same three curves are found also at 40°.

TABLE 5

Amount (% by weight)			Total amt. of salts (% by weight)	Composition of solid phase (% by weight)		Solid phases
LiCl	$ZnCl_2$	H_2O		LiCl	$ZnCl_2$	
			25° Isotherm			
–	81.20	18.80	81.20	–	–	
3.65	76.18	20.17	79.83	3.58	76.21	
6.25	72.46	21.29	78.71	–	–	$ZnCl_2 \cdot 1.5H_2O$
9.10	68.23	22.67	77.33	9.40	68.34	
11.28	65.30	23.42	76.58	–	–	
14.71	60.62	24.67	75.33	15.17	61.89	$ZnCl_2 \cdot 1.5H_2O + ZnCl_2 \cdot 2LiCl \cdot 2.5H_2O$
17.36	58.42	24.22	75.78	22.10	56.14	
20.05	53.86	26.09	73.91	25.07	52.53	
23.46	49.61	26.93	73.07	27.26	50.11	$ZnCl_2 \cdot 2LiCl \cdot 2.5H_2O$
25.27	46.48	28.25	71.75	29.59	48.06	
29.12	41.40	29.48	70.52	30.71	46.12	
30.51	38.87	30.62	69.38	–	–	$ZnCl_2 \cdot 2LiCl \cdot 2.5H_2O + LiCl \cdot H_2O$
32.47	33.48	34.05	65.95	19.18	49.10	
34.60	27.20	38.20	61.80	15.10	50.92	
36.50	20.90	42.60	54.40	15.41	50.18	
39.19	15.18	45.63	54.37	6.89	56.46	$LiCl \cdot H_2O$
41.43	9.17	49.40	50.60	4.53	57.15	
43.20	5.64	51.16	48.84	2.62	59.60	
45.95	–	54.05	45.95	–	–	
			40° Isotherm			
–	81.86	18.14	81.86	–	–	
4.21	77.13	18.66	81.34	4.30	77.26	
10.46	69.50	20.04	79.96	10.26	69.71	$ZnCl_2$
15.48	64.31	20.21	79.79	16.14	65.67	
19.56	60.07	20.37	79.63	20.12	61.10	$ZnCl_2 + ZnCl_2 \cdot 2LiCl \cdot 2.5H_2O$
20.62	57.48	21.90	78.10	27.18	54.50	$ZnCl_2 \cdot 2LiCl \cdot 2.5H_2O$
29.60	43.42	26.98	73.02	–	–	$ZnCl_2 \cdot 2LiCl \cdot 2.5H_2O + LiCl \cdot H_2O$
30.16	39.60	30.24	69.76	47.13	23.32	
30.68	25.16	44.16	55.84	52.26	13.10	$LiCl \cdot H_2O$
41.65	12.90	45.45	54.55	59.34	4.62	
47.98	–	52.02	47.98	–	–	

The compound obtained $ZnCl_2 \cdot 2LiCl \cdot 2.5H_2O$ resembles crystals of the rhombic syngony in external habit (Fig. 6) [see plate, page 342] and is highly hygroscopic. It is difficult to dry out the crystals in a desiccator over sulfuric acid, or even over phosphoric anhydride; they readily dissolve in alcohol, and they readily hydrate in air. In order to confirm the composition of this compound, we prepared a synthetic solution corresponding approximately to the compound, and then evaporated it isothermally under reduced pressure. The first crystals that appeared were rapidly separated and dried in a desiccator over sulfuric acid. Analysis of the crystals gave the following results:

Found %: $ZnCl_2$ 50.56; LiCl 32.47; H_2O 16.97.
$ZnCl_2 \cdot 2LiCl \cdot 2.5H_2O$. Calculated %: $ZnCl_2$ 51.22; LiCl 31.87; H_2O 16.91.

The 40° isotherm confirmed the presence of the compound obtained at 25°. The solubility of lithium chloride changes very little in presence of increasing amounts of $ZnCl_2$ right up to the point at which the compound is formed.

The 25° and 40° isotherms of the system $LiCl-CdCl_2-H_2O$ (Table 6, Fig. 7). Increase in the concentration of cadmium chloride led to rise in the viscosity of the solutions, and increase in the LiCl concentration of the solutions accelerated settling in the liquid phase. The same phenomenon occurred also in the preceding system. There are three curves in Fig. 7: AB, the crystallization curve for lithium chloride monohydrate; BC, the crystallization curve of the chemical compound $LiCl \cdot CdCl_2 \cdot 2.5H_2O$; and CD, the crystallization curve for the corresponding cadmium chloride hydrate. The length of the curve for the crystallization of the double compound is reduced at 40°.

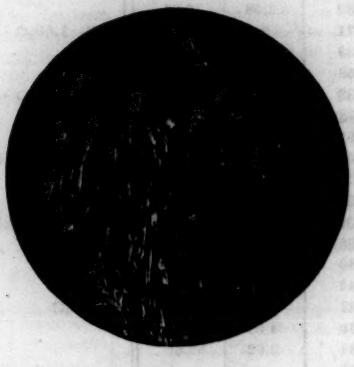

Fig. 6.

Fig. 8

TABLE 6

Amount (% by weight)			Total amt. of salts (% by weight)	Composition of solid phase (% by weight)		Solid phases
LiCl	$CdCl_2$	H_2O		LiCl	$CdCl_2$	
			25° Isotherm			
45.95	–	54.05	45.95	–	–	
44.20	2.02	53.78	46.22	55.40	1.62	$LiCl \cdot H_2O$
42.31	6.48	51.21	48.79	53.54	3.25	
41.43	9.63	48.94	51.06	53.26	5.24	
39.61	13.00	47.39	52.61	–	–	$LiCl \cdot H_2O + LiCl \cdot CdCl_2 \cdot 2.5H_2O$
37.60	15.14	47.26	52.74	26.12	44.38	
32.68	18.96	48.36	51.64	22.95	47.53	$LiCl \cdot CdCl_2 \cdot 2.5H_2O$
28.12	24.04	47.84	52.16	20.84	50.61	
25.07	27.80	47.13	52.87	21.16	50.47	
19.96	34.25	45.79	54.21	17.83	52.60	
17.40	37.68	44.92	55.08	16.10	55.37	$LiCl \cdot CdCl_2 \cdot 2.5H_2O$
14.28	42.55	43.17	56.83	15.48	56.86	
12.63	46.07	41.30	58.70	13.68	58.74	
10.54	49.12	40.34	59.66	–	–	$CdCl_2 \cdot 2.5H_2O + LiCl \cdot CdCl_2 \cdot 2.5H_2O$
7.20	52.51	40.29	59.71	4.10	66.15	
3.12	55.82	41.06	58.94	1.79	69.53	$CdCl_2 \cdot 2.5H_2O$
–	59.48	40.52	59.48	–	–	
			40° Isotherm			
47.98	–	52.02	47.98	–	–	
45.35	4.26	50.39	49.61	56.23	2.50	$LiCl \cdot H_2O$
39.74	15.30	44.96	55.04	54.05	8.22	
38.86	18.12	43.02	56.98	–	–	$LiCl \cdot H_2O + LiCl \cdot CdCl_2 \cdot 2.5H_2O$
37.50	19.51	42.99	57.01	25.02	47.43	
28.13	28.39	43.48	56.52	20.18	53.07	$LiCl \cdot CdCl_2 \cdot 2.5H_2O$
17.38	39.67	42.95	57.05	17.34	56.70	
15.57	42.20	42.23	57.77	–	–	$CdCl_2 \cdot H_2O + LiCl \cdot CdCl \cdot 2.5H_2O$
13.08	45.15	41.77	58.23	5.43	71.48	
4.28	55.47	40.25	59.75	2.25	73.59	
–	62.14	37.86	62.14	–	–	$CdCl_2 \cdot H_2O$

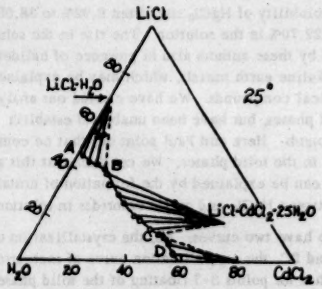

Fig. 7

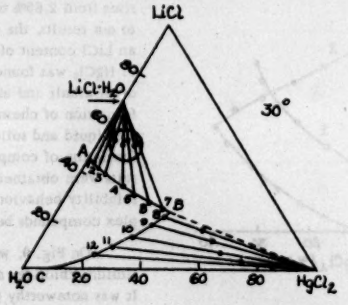

Fig. 9

By a method similar to that used for the preparation of crystals of $ZnCl_2 \cdot 2LiCl \cdot 2.5H_2O$ we prepared also some well formed clear crystals of the compound $LiCl \cdot CdCl_2 \cdot 2.5H_2O$ (Fig. 8), which were decomposed by alcohol to the component substances.

This compound decomposes when exposed to the air, but more slowly than the analogous zinc chloride compound. Analysis of the crystals gave the following results:

Found %: LiCl 14.95; $CdCl_2$ 66.87; H_2O 18.22

$LiCl \cdot CdCl_2 \cdot 2.5H_2O$. Calculated %: LiCl 15.66; CdCl 67.71; H_2O 16.63

In external habit, the crystals belong to the monoclinic syngony, which is characteristic for $CdCl_2 \cdot 2.5H_2O$.

The 30° isotherm of the system $LiCl-HgCl_2-H_2O$ (Table 7, Fig. 9). The solubility of mercury halides in presence of chlorides of the alkali and alkaline earth metals has been studied by Herz and Paul [9]. These authors precipitated mercury ions with hydrogen sulfide. The chlorine was titrated with silver nitrate in presence of potassium chromate as indicator. We have used this method of analysis, but obtained low results. We, therefore, preferred to carry out the analysis for mercury ions by Korenman's method [6] and determine chlorine only gravimetrically.

TABLE 7

Amount (% by weight)			Total amt. of salts (% by weight)	Composition of solid phase (% by weight)		Solid phases
LiCl	$HgCl_2$	H_2O		LiCl	$HgCl_2$	
47.16	–	52.84	47.16	–	–	$LiCl \cdot H_2O$
44.05	2.53	53.42	46.58	57.83	1.46	
41.48	5.61	52.91	47.09	57.12	3.06	
38.47	9.62	51.91	48.09	53.16	5.54	
34.10	16.07	49.83	50.17	51.25	9.13	
30.39	22.50	47.11	52.89	53.28	10.20	
27.03	29.24	43.73	56.27	50.17	14.32	
23.90	36.08	40.02	59.98	52.18	15.74	
22.70	38.05	39.25	60.75	–	–	$LiCl \cdot H_2O + HgCl_2$
21.66	37.80	40.54	59.46	16.47	53.06	$HgCl_2$
18.21	35.29	46.50	53.50	11.35	54.13	
14.07	31.22	54.71	45.29	7.60	63.54	
8.60	25.53	65.87	34.13	3.24	73.09	
5.36	21.75	72.89	27.11	1.86	84.47	
–	6.92	93.08	6.92	–	–	

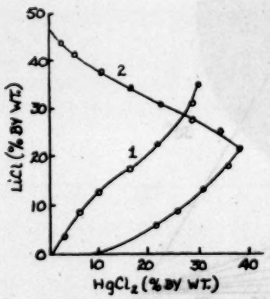

Fig. 10. 1) According to Herz and Paul at 25°; 2) according to our results at 30°.

According to Herz and Paul's results, the solubility of $HgCl_2$ rises from 2.65% to 30.62% at an LiCl content of 35.27%. According to our results, the solubility of $HgCl_2$ rises from 6.92% to 38.05% at an LiCl content of 22.70% in the solution. The rise in the solubility of $HgCl_2$ was found by these authors also in presence of halides of other alkali and alkaline earth metals, which may be explained by the formation of chemical compounds. We have carried out analyses on the liquid and solid phases, but have been unable to establish the formation of compounds. Herz and Paul point out that no complex salts were obtained in the solid phases. We consider that this anomalous solubility behavior can be explained by the formation of unstable complex compounds between $HgCl_2$ and metal chlorides in solution.

On Fig. 9, we have two curves: AB, the crystallization curve of lithium chloride; and BC, the crystallization curve of mercuric chloride. It was noteworthy that for points 3-7 floating of the solid phase occurred; after long stirring it gradually fell to the bottom of the reaction vessel. This is to be explained by the fact that the density of the solution was slightly higher than that of LiCl; thus, we found the density of the liquid phase for point 7 to be 2.077, and the density of LiCl is 2.074.

Fig. 10 shows liquidus curves for the system $LiCl-HgCl_2-H_2O$. Curve 1 represents the results of Herz and Paul at 25°, and Curve 2 represents our results at 30°. As will be seen, the solubility of $HgCl_2$ increases with rise in temperature and increase in the concentration of LiCl up to a certain limit.

SUMMARY

1. Ternary aqueous systems containing lithium chloride and chlorides of Group II metals have been studied by the isothermal method.

2. In the systems $LiCl-BeCl_2-H_2O$, $LiCl-CaCl_2-H_2O$, $LiCl-SrCl_2-H_2O$ and $LiCl-BaCl_2-H_2O$, no chemical compounds are formed between the components.

3. In the systems $LiCl-ZnCl_2-H_2O$ and $LiCl-CdCl_2-H_2O$, the chemical compounds $ZnCl_2 \cdot 2LiCl \cdot 2,5H_2O$ and $LiCl \cdot CdCl_2 \cdot 2,5H_2O$ have been found.

4. In the system $LiCl-HgCl_2-H_2O$ the solubility of $HgCl_2$ is enhanced in presence of LiCl. No chemical compounds between the components were found.

Received July 11, 1953

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SYNTHESIS OF ARYLSTIBONIC ACIDS VIA DOUBLE SALTS OF DIAZONIUM SALTS AND ANTIMONY PENTACHLORIDE

A. N. Nesmeyanov, O. A. Reutov, and P. G. Knol

The double salts of diazonium salts and antimony pentachloride, which have been synthesized by one of us [1], can act as starting materials for the preparation of organoantimony compounds of various types. Thus it has been shown previously [2] that, when these double diazonium-antimony salts are decomposed with iron powder, high yields of compounds of the types Ar_2SbCl_3 and Ar_3SbCl_2 are obtained in accordance with the following equations:

$$2ArN_2Cl \cdot SbCl_5 + 3Fe \rightarrow Ar_2SbCl_3 + 2N_2 + SbCl_3 + 3FeCl_2. \quad (1)$$

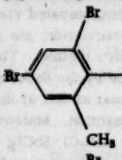
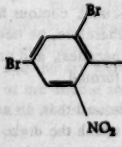
$$3ArN_2Cl \cdot SbCl_5 + 5Fe \rightarrow Ar_3SbCl_2 + 3N_2 + 2SbCl_3 + 5FeCl_2. \quad (2)$$

In the present investigation it has been shown that, when the double salts of diazonium salts and antimony pentachloride are decomposed with copper, arylstibonic acids are formed. The synthesis of arylstibonic acids was carried out in three stages: 1) preparation of the double diazonium salts of ferric chloride, 2) preparation of the double diazonium salts of antimony pentachloride, and 3) decomposition of the double diazonium salts of antimony pentachloride.

The preparation of the double diazonium salts of ferric chloride was carried out by the procedure developed by one of us and Kocheshkov [3], with small modifications indicated in the experimental part. Compounds of this type prepared for the first time are given in Table 1.

TABLE 1

Double Diazonium Salts of Ferric Chloride

Formula	M.P. (decomp.) (in °C)	Color	Yield (%)
o-$CH_3OC_6H_4N_2Cl \cdot FeCl_3$	70	Yellow	54
p-$CH_3OC_6H_4N_2Cl \cdot FeCl_3$	78	"	63
o-$C_2H_5OC_6H_4N_2Cl \cdot FeCl_3$	56	"	45
p-$C_2H_5OC_6H_4N_2Cl \cdot FeCl_3$	40	"	67
2,4-$(CH_3)_2C_6H_3N_2Cl \cdot FeCl_3$	45-46	"	80
p-$CNSC_6H_4N_2Cl \cdot FeCl_3$	88	"	30
α-$C_{10}H_7N_2Cl \cdot FeCl_3$	75-77	"	73
β-$C_{10}H_7N_2Cl \cdot FeCl_3$	78-79	"	87
p,p'-$FeCl_3 \cdot ClN_2C_6H_4-C_6H_4N_2Cl \cdot FeCl_3$	97-98	"	86
	84	"	95
	45-46	"	50

The synthesis of the double diazonium salts of antimony pentachloride was carried out by the procedure described by one of us [1]. The following double salts were obtained for the first time: the salts formed by antimony pentachloride with 2,4-dibromo-6-methylbenzenediazonium chloride (m.p. 138°, yield 93%), with p-methoxybenzenediazonium chloride (m.p. 129°, yield 59%), with o-ethoxybenzenediazonium chloride (m.p. 110°, yield 33%), and with p-ethoxybenzenediazonium chloride (m.p. 106°, yield 86%).

The decomposition of the double diazonium salts of antimony pentachloride was carried out in an acetone medium according to the equation:

$$ArN_2Cl \cdot SbCl_5 + Cu_2Cl_2 \rightarrow ArSbCl_4 + N_2 + 2CuCl_2.$$

The arylantimony tetrachloride was hydrolyzed with aqueous caustic soda and isolated in the form of the arylstibonic acid.

The effect of reaction conditions on the yield was investigated in detail in the case of the synthesis of phenylstibonic acid. The results of these experiments are given in Table 2.

TABLE 2

Effect of Reaction Conditions on the Yield of Phenylstibonic Acid

Amount of $C_6H_5N_2Cl \cdot SbCl_5$, in g	Amount of Cu_2Cl_2, in g	Amount of solvent (ml)	Reaction temp. (°C)	Duration of reaction (hr.)	Yield of phenylstibonic acid	
					in g	(% of theoretical)
10	15	Acetone (100)	25	6	2.6	37
20	43	" (90)	25	44	2.4	17
5	20	" (60)	56	2	0.8	22
5	10	" (60)	25	4	1.2	34
5	10	Methanol (60)	30	24	0.25	7
5	8	Chloroform (100)	25	96	0.22	6
5	8	Glacial acetic acid (60)	25	(including 4 hrs. at 60°)	0.1	3
5	8	Dioxane (50)	25	8	0.6	17
4.3	8	Methyl acetate (50)	25	5	1.2	39

It will be seen from Table 2 that the optimum conditions for the synthesis of phenylstibonic acid obtain when the double diazonium salt of antimony pentachloride is decomposed with a two- or three-fold excess of cuprous chloride at 25-30° for 4-5 hours in an acetone or methyl acetate medium.

The results of the syntheses of certain other arylstibonic acids [4] are given in Table 3 (the yields of the same substances prepared by Schmidt's reaction are given in parentheses).

TABLE 3

Yields of Arylstibonic Acids

Formula	Yield (% of theoretical amt.)
$C_6H_5SbO(OH)_2$	39 (40-60)
$p\text{-}CH_3C_6H_4SbO(OH)_2$	30 (40)
$2,4\text{-}(CH_3)_2C_6H_3SbO(OH)_2$	14 –
$o\text{-}O_2NC_6H_4SbO(OH)_2$	1 –
$m\text{-}O_2NC_6H_4SbO(OH)_2$	6 –
$p\text{-}O_2NC_6H_4SbO(OH)_2$	12 (11)
$o\text{-}ClC_6H_4SbO(OH)_2$	1 –
$p\text{-}ClC_6H_4SbO(OH)_2$	5 (38)
$p\text{-}BrC_6H_4SbO(OH)_2$	1 (14)
$p\text{-}IC_6H_4SbO(OH)_2$	9 (5)
$p\text{-}CH_3OC_6H_4SbO(OH)_2$	4 (31)
$o\text{-}C_2H_5OC_6H_4SbO(OH)_2$	4 –
$p\text{-}C_2H_5OC_6H_4SbO(OH)_2$	3 –
$\alpha\text{-}C_{10}H_7SbO(OH)_2$	4 –
$\beta\text{-}C_{10}H_7SbO(OH)_2$	8 (2)

In a number of cases (phenyl-, p-tolyl-, p-iodophenyl-, p-nitropheny-, and 2-naphthyl-stibonic acids) this method of preparation by the decomposition of double diazonium salts of antimony pentachloride can compete successfully with Schmidt's method [5]. The yields of phenyl-, p-iodophenyl-, p-nitrophenyl-, and p-tolyl-stibonic acids, prepared via the double diazonium salts of antimony pentachloride, are not inferior to the yields attained by Schmidt's method. The yield of 2-naphthylstibonic acid prepared by the decomposition of $ArN_2Cl \cdot SbCl_5$ is four times as great as that of the same substance prepared by Schmidt's reaction. Moreover, in the synthesis of arylstibonic acids via $ArN_2Cl \cdot SbCl_5$, as opposed to the synthesis by Schmidt's method, copious foam formation does not occur (and there is, therefore, no need to use reaction vessels having enormous capacities), and precipitates causing difficult filtration are not formed.

Investigation of the by-products showed that, in addition to arylstibonic acids, substances in which the diazo group was replaced by halogen were formed. Thus, after decomposition

of the double salt of antimony pentachloride with p-iodobenzenediazonium chloride, 1-chloro-4-iodobenzene was isolated. In other cases, 1-chloro-2-nitrobenzene, 3,5-dibromo-2-chlorotoluene, etc., were isolated correspondingly. Formation of products of the replacement of the diazo group by hydrogen practically did not occur, a fact that allows us to infer that the reaction studied is of homolytic, not free-radical, character.

EXPERIMENTAL

1. Preparation of the Double Diazonium Salts of Ferric Chloride

The experiments were performed under the conditions indicated by Kocheshkov and Nesmeyanov [3], with slight modifications: the ferric chloride (three-fold excess) was dissolved in the minimum amount of water at 50-60°, and the solution was then cooled to −5° and poured into a cold solution of the diazotized amine. The double diazonium salt of ferric chloride was precipitated by addition of concentrated HCl to the stirred solution. With this procedure precipitation of the double salt readily occurred already at temperatures of 0-5°. The double salts so obtained were dried in the air and, when necessary, purified by reprecipitation from acetone with ether.

By means of this procedure the following double salts were prepared for the first time: the double salts of ferric chloride with o-methoxybenzenediazonium chloride (m.p. 70°, yield 54%), with p-methoxybenzenediazonium chloride (m.p. 78°, yield 63%), with o-ethoxybenzenediazonium chloride (m.p. 56°, yield 45%), with p-ethoxybenzenediazonium chloride (m.p. 40°, yield 67%), with 2,4-dimethylbenzenediazonium chloride (m.p. 45-46°, yield 80%), with p-thiocyanatobenzenediazonium chloride (m.p. 88°, yield 30%), with 2-naphthalenediazonium chloride (m.p. 75-77°, yield 73%), with 1-naphthalenediazonium chloride (m.p. 78-79°, yield 87%), with tetrazotized benzidine (m.p. 97-98°, yield 86%), with 2,4-dibromo-6-methylbenzenediazonium chloride (m.p. 84°, yield 95%), and with 2,4-dibromo-6-nitrobenzenediazonium chloride (m.p. 45-46°, yield 50%). All of these double salts are yellow crystalline substances that melt with decomposition (the double salt of ferric chloride with tetrazotized benzidine melts with an explosion). With a few exceptions, these substances are stable to storage in air for several weeks.

2. Preparation of the Double Diazonium Salts of Antimony Pentachloride

The preparation was carried out by the procedure developed by one of us [1]. The following substances have been synthesized for the first time:

Double salt of antimony pentachloride with 2,4 dibromo-6-methylbenzenediazonium chloride, yield 93%, colorless crystals, m.p. 138° with decomposition.

	Found %:	N 4.91; 4.89
$CH_3Br_2C_6H_2N_2Cl \cdot SbCl_5$.	Calculated %:	N 4.57

Double salt of antimony pentachloride with p-methoxybenzenediazonium chloride, yield 59%, pinkish crystals, m.p. 129° with decomposition.

	Found %:	N 6.53; 6.43
$CH_3OC_6H_4N_2Cl \cdot SbCl_5$.	Calculated %:	N 6.44

Double salt of antimony pentachloride with o-ethoxybenzenediazonium chloride, yield 33%, pinkish crystals, m.p. 110° with decomposition.

	Found %:	N 6.25; 6.24
$C_2H_5OC_6H_4N_2Cl \cdot SbCl_5$.	Calculated %:	N 6.23

Double salt of antimony pentachloride with p-ethoxybenzenediazonium chloride, yield 86%, pinkish crystals, m.p. 106° with decomposition.

	Found %:	N 6.07; 6.17
$C_2H_5OC_6H_4N_2Cl \cdot SbCl_5$.	Calculated %:	N 6.23

In the syntheses of the last three substances, certain complications arose: when attempts were made to precipitate the substance with ether under the usual conditions [1], no precipitate formed; instead, two layers were formed — an oily layer and an ethereal layer. The reaction mixture (both layers) was evaporated down under reduced pressure, and the dry residue was reprecipitated from acetone with ether in order to purify it from ferric chloride. In the case of the double salts containing alkoxyphenyl radicals, still purer products were obtained by reprecipitation from methanol with concentrated hydrochloric acid.

3. Synthesis of Arylstibonic Acids

Synthesis of Phenylstibonic Acid. a) The double salt of benzenediazonium chloride 10 g (0.0228 mole) was mixed with cuprous chloride 15 g (0.09 mole). The mixture was placed in a flask, 100 ml of acetone* was added, and the contents were stirred for six hours at 25°. The solvent was distilled off, and the residue was ground with 80 ml of 5 N NaOH. After two hours, the insoluble residue was filtered off and washed with 5 N NaOH. The filtrate was acidified to Congo red with 5 N HCl. The precipitated phenylstibonic acid was filtered off, washed well with water, and dried at 80-90° (yield 2.6 g, i.e., 37%). The substance was dissolved in concentrated hydrochloric acid and converted by addition of a solution of pyridine in hydrochloric acid into the pyridine complex $C_6H_5SbCl_4 \cdot C_5H_5N \cdot HCl$, m.p. 133° (after crystallization from alcohol) the literature [6] gives m.p. 139°).

	Found %:	N 3.40; 3.42
$C_6H_5SbCl_4 \cdot C_5H_5N \cdot HCl$.	Calculated %:	N 3.07

The phenylstibonic acid was converted also into the quinoline complex, which melted at 207° after crystallization from alcohol.

	Found %:	N 2.98; 3.09
$C_6H_5SbCl_4 \cdot C_9H_7N \cdot HCl$.	Calculated %:	N 2.77

b) When the reaction was carried out between 20 g (0.0456 mole) of the double salt of benzenediazonium chloride with antimony tetrachloride and 43 g (0.217 mole) of cuprous chloride in 90 ml of acetone at 25° for 44 hours, 2.4 g (17%) of phenylstibonic acid was obtained.

c) When 5 g (0.0114 mole) of the double salt of benzenediazonium chloride with antimony pentachloride was decomposed with 20 g (0.1 mole) of cuprous chloride in 60 ml of acetone at 56° for two hours, 0.8 g (22%) of phenylstibonic acid was obtained.

d) When 5 g (0.0114 mole) of the double salt of benzenediazonium chloride with antimony pentachloride was decomposed with 10 g (0.05 mole) of cuprous chloride in 60 ml of acetone at 25° for four hours, 1.2 g (34%) of phenylstibonic acid was obtained.

e) When 5 g (0.0114 mole) of the double salt of benzenediazonium chloride with antimony pentachloride was decomposed with 10 g (0.05 mole) of cuprous chloride in 60 ml of methanol at 30° for 24 hours, 0.25 g (7%) of phenylstibonic acid was obtained.

f) When 5 g (0.0114 mole) of the double salt was decomposed with 8 g (0.04 mole) of cuprous chloride in 100 ml of chloroform at 25° for 96 hours, 0.22 g (6%) of phenylstibonic acid was obtained.

g) When 5 g (0.0114 mole) of the double salt was decomposed with 8 g (0.04 mole) of cuprous chloride in 60 ml of glacial acetic acid for 92 hours at 25° and then for four hours at 60°, 0.1 g (3%) of phenylstibonic acid was obtained.

h) When 5 g (0.0114 mole) of the double salt was decomposed with 8 g (0.04 mole) of cuprous chloride in 50 ml of dioxane at 25° for eight hours, 0.6 g (17%) of phenylstibonic acid was obtained.

i) When 4.3 g (0.0098 mole) of the double salt was decomposed with 8 g (0.04 mole) of cuprous chloride in 50 ml of methyl acetate at 25° for five hours, 1.2 g (39%) of phenylstibonic acid was obtained.

Synthesis of p-Tolylstibonic Acid. a) The double salt of p-toluenediazonium chloride with antimony pentachloride 3.5 g (0.0077 mole) was decomposed with 7 g (0.035 mole) of cuprous chloride in 75 ml of acetone at 25° for six hours. The solvent was distilled off, and the residue was ground with 35 ml of 5 N NaOH. After two hours, the undissolved residue was filtered off and washed with 5 N NaOH. The filtrate was acidified to Congo red with 5 N HCl. The precipitated p-tolylstibonic acid was filtered off, well-washed with water, and dried at 70-80°. (Yield 0.65 g, i.e., 26%).

The p-tolylstibonic acid was converted into the pyridine complex, which melted after crystallization from alcohol, at 176-178° (the literature [6] gives 180°).

	Found %:	N 3.03; 3.00
$CH_3C_6H_4SbCl_4 \cdot C_5H_5N \cdot HCl$.	Calculated %:	N 2.90

b) When 5 g (0.011 mole) of the double salt of p-toluenediazonium chloride with antimony pentachloride was decomposed with 9 g (0.045 mole) of cuprous chloride in 75 ml acetone at 56° for three hours, only traces of

* Once-distilled commercial acetone was used.

p-tolylstibonic acid were obtained.

c) When 5 g (0.011 mole) of the double salt of p-toluenediazonium chloride with antimony pentachloride was decomposed with 9 g (0.045 mole) of cuprous chloride in 50 ml of methyl acetate at 25° for five hours, 1.1 g (30%) of p-tolylstibonic acid was obtained.

Synthesis of p-Nitrophenylstibonic Acid. a) When 2.8 g (0.0058 mole) of the double salt of p-nitrobenzenediazonium chloride with antimony pentachloride was treated as in the previous experiments with 8 g (0.04 mole) of cuprous chloride in 60 ml of acetone at 56° for two hours, 0.25 g (12%) of p-nitrophenylstibonic acid was obtained. The stibonic acid was converted into its pyridine complex, which melted, after two crystallizations from alcohol, at 167-168° (the literature [6] gives 168.5°).

Found %: N 5.70; 5.52

$O_2NC_6H_4SbCl_4 \cdot C_5H_5N \cdot HCl$. Calculated %: N 5.59

b) When 5 g (0.01 mole) of the double salt of p-nitrobenzenediazonium chloride with antimony pentachloride was decomposed with 8 g (0.04 mole) of cuprous chloride in 50 ml of acetone at 25° for five hours, 0.15 g (4%) of p-nitrophenylstibonic acid was obtained.

Synthesis of m-Nitrophenylstibonic Acid. When 10 g (0.02 mole) of the double salt of m-nitrobenzenediazonium chloride with antimony pentachloride was decomposed with 6 g (0.03 mole) of cuprous chloride in 60 ml of acetone at 25° for 14 hours, 0.47 g (6%) of m-nitrophenylstibonic acid was obtained. The stibonic acid was converted into its pyridine complex, which melted, after two crystallizations from alcohol, at 187° (the literature [6] gives 187°).

Synthesis of o-Nitrophenylstibonic Acid. When 17.7 g (0.036 mole) of the double salt of o-nitrobenzenediazonium chloride with antimony pentachloride was decomposed with 22.3 g (0.13 mole) of cuprous chloride in 80 ml of acetone at 25° for six hours, 0.1 g (1.0%) of o-nitrophenylstibonic acid was obtained. The residue obtained after treatment of the reaction mixture with alkali and removal of the alkaline solution of the stibonic acid by filtration was dried and thoroughly extracted with ether. The ether extract was dried with calcium chloride, and the ether was evaporated off. The residue was 1-chloro-2-nitrobenzene; m.p. after recrystallization from alcohol 31° (the literature [7] gives 32.5°).

Synthesis of p-Chlorophenylstibonic Acid. When 10 g (0.025 mole) of the double salt of p-chlorobenzenediazonium chloride with antimony pentachloride was decomposed with 15 g (0.09 mole) of cuprous chloride in 60 ml of acetone at 25° for six hours, 0.35 g (5%) of p-chlorophenylstibonic acid was obtained.

Synthesis of o-Chlorophenylstibonic Acid. When 5.2 g (0.013 mole) of the double salt of o-chlorobenzenediazonium chloride with antimony pentachloride was decomposed with 8 g (0.04 mole) of cuprous chloride in 50 ml of acetone at 25° for six hours, 0.05 g (1%) of o-chlorophenylstibonic acid was obtained.

Synthesis of p-Bromophenylstibonic Acid. When 5 g (0.011 mole) of the double salt of p-bromobenzenediazonium chloride with antimony pentachloride was decomposed with 7 g (0.035 mole) of cuprous chloride in 50 ml of acetone at 25° for six hours, 0.05 g (1%) of p-bromophenylstibonic acid was obtained.

Synthesis of p-Iodophenylstibonic Acid. When 10 g (0.02 mole) of the double salt of p-iodobenzenediazonium chloride with antimony pentachloride was decomposed with 15 g (0.075 mole) of cuprous chloride in 60 ml of acetone at 25° for six hours, 0.75 g (9%) of p-iodophenylstibonic acid was obtained. The residue obtained after treatment of the reaction mixture with alkali and removal of the alkaline solution of the stibonic acid by filtration was extracted three times with 30-ml portions of ether. The ether solution was dried with calcium chloride, and the ether was evaporated off. The residue, 1-chloro-4-iodobenzene, was recrystallized from alcohol; m.p. 54° (the literature [8] gives 56°). The yield was 1.2 g (28%).

Synthesis of p-Methoxyphenylstibonic Acid. When 5 g (0.013 mole) of the double salt of p-methoxybenenediazonium chloride with antimony pentachloride was decomposed with 7 g (0.035 mole) of cuprous chloride in 50 ml of acetone at 25° for six hours, 0.15 g (4%) of p-methoxyphenylstibonic acid was obtained.

Synthesis of p-Ethoxyphenylstibonic Acid. When 15 g (0.038 mole) of the double salt of p-ethoxybenzenediazonium chloride with antimony pentachloride was decomposed with 12 g (0.06 mole) of cuprous chloride in 80 ml of acetone at 25° for five hours, 0.3 g (3%) of p-ethoxyphenylstibonic acid was obtained.

Synthesis of o-Ethoxyphenylstibonic Acid. When 5 g (0.013 mole) of the double salt of o-ethoxybenzenediazonium chloride with antimony pentachloride was decomposed with 7 g (0.035 mole) of cuprous chloride in 50 ml of acetone at 25° for six hours, 0.15 g (4%) of o-ethoxyphenylstibonic acid was obtained.

Synthesis of 2,4-Dimethylphenylstibonic Acid. When 7.5 g (0.024 mole) of the double salt of 2,4-dimethylbenzenediazonium chloride with antimony pentachloride was decomposed with 6 g (0.03 mole) of cuprous chloride in 60 ml of acetone at 25° for eight hours, 0.75 g (14%) of 2,4-dimethylphenylstibonic acid was obtained.

Synthesis of 1-Naphthylstibonic Acid. When 3.5 g (0.007 mole) of the double salt of 1-naphthalenediazonium chloride with antimony pentachloride was decomposed with 3 g (0.015 mole) in 50 ml of acetone at 25° for five hours, 0.1 g (4%) of 1-naphthylstibonic acid was obtained. The 1-naphthylstibonic acid was converted into its pyridine complex, pale-yellow crystals of m.p. 186-188° (the literature [9] gives 187-189°).

Synthesis of 2-Naphthylstibonic Acid. a) When 3 g (0.006 mole) of the double salt of 2-naphthalenediazonium chloride with antimony pentachloride was decomposed with 5 g (0.025 mole) of cuprous chloride in 50 ml of acetone at 25° for four hours, and the reaction mixture was treated in the usual way, 0.18 g (8 %) of 2-naphthylstibonic acid was obtained. The 2-naphthylstibonic acid was converted in the usual way into its pyridine complex $C_{18}H_7SbCl_4 \cdot C_5H_5N \cdot HCl$, which, after being crystallized from alcohol, was a yellow substance of m.p. 199-200° (according to the literature [9] it is a yellow substance, m.p. 200-202°).

	Found %:	N 2.75; 2.74
$C_{18}H_7SbCl_4 \cdot C_5H_5N \cdot HCl$.	Calculated %:	N 2.76

2-Naphthylstibonic acid was converted also into its quinoline complex, which, after being crystallized from alcohol, was a yellow substance, m.p. 183° with decomposition (according to the literature [9] it is a yellow substance, m.p. 174-176° with decomposition).

	Found %:	C 41.24; 41.24; H 3.05; 3.04; N 2.72; 2.60
$C_{18}H_7SbCl_4 \cdot C_9H_7N \cdot HCl$.	Calculated %:	C 41.00 H 2.70; N 2.52

b) When 5.3 g (0.0108 mole) of the double salt of 2-naphthalenediazonium chloride was decomposed with 9 g (0.045 mole) of cuprous chloride in 50 ml of methyl acetate at 25° for nine hours, 0.3 g (7%) of 2-naphthylstibonic acid was obtained.

Decomposition of the Double Salt of 2,4-Dibromo-6-methylbenzenediazonium Chloride with Antimony Pentachloride by means of Cuprous Chloride. When 10.0 g of the double salt of 2,4-dibromo-6-methylbenzenediazonium chloride with antimony pentachloride was decomposed with excess of cuprous chloride, the corresponding arylstibonic acid was not formed. Treatment of the reaction mixture as in the preceding experiment yielded 0.8 g of 3,5-dibromo-2-chlorotoluene as colorless crystals of m.p. 53°, soluble in ether, alcohol, and acetone.

	Found %:	C 29.22; H 1.74
$CH_3C_6H_2Br_2Cl$.	Calculated %:	C 29.45; H 1.75

This substance is described for the first time.

SUMMARY

1. A study has been made of the decomposition, in an organic medium in presence of cuprous chloride, of the double salts formed by diazonium salts with antimony pentachloride; the reaction results in the formation of arylstibonic acids.

2. In a number of cases (phenyl-, p-tolyl-, p-nitrophenyl-, p-iodophenyl-, and 2-naphthyl-stibonic acids) this reaction can successfully compete with the Bart-Schmidt-Scheller method for the synthesis of arylstibonic acids.

3. The nature of the by-products of the reaction indicates that the process is of a homolytic, not free-radical, character.

Received July 1, 1953

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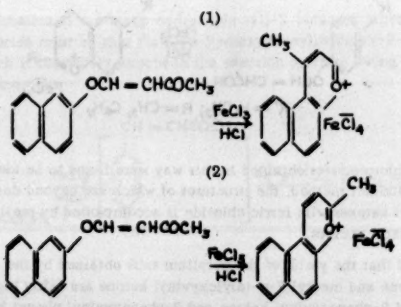
REARRANGEMENT OF 2-PHENOXYVINYL KETONES

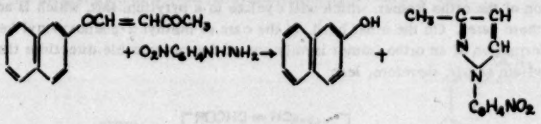
A. N. Nesmeyanov, N. K. Kochetkov, and M. I. Rybinskaya

By the action of phenols on 2-chlorovinyl ketones in an alkaline medium, we have recently [1] prepared 2-phenoxyvinyl ketones, the properties of which have received very little study. In this paper, we describe one of the reactions of 2-phenoxyvinyl ketones, which occurs when they are treated with ferric chloride or similar reagent.

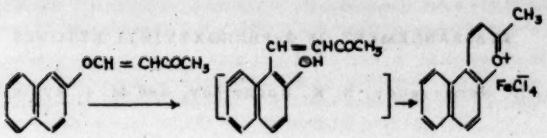
As we wished to extend the new medium for the synthesis of pyrylium salts that we have recently developed [2], we have studied the reaction of 2-phenoxyvinyl ketones with ferric chloride in the hope of obtaining naphtho- and benzo-pyrylium salts having a radical in the 4-position of the pyrylium ring. When methyl 2-(2-naphthyloxy) vinyl ketone [4-(2-naphthyloxy)-3-buten-2-one] was treated with ferric chloride in a mixture of hydrochloric and acetic acids, a methylnaphthopyrylium chloroferrate (III) was indeed formed. It was found unexpectedly, however, that the substance obtained was not a 1-methylnaphtho[2,1-b]pyrylium salt, but was 3-methylnaphtho[2,1-b] pyrylium chloroferrate (III), a fact that was established by comparison of the substance obtained with an authentic sample of the 3-methylnaphtho[2,1-b]pyrylium salt, the structure of which we have already established [2]. Hence, the reaction of methyl 2-(2-naphthyloxy)vinyl ketone with ferric chloride proceeds not by Scheme 1, but by Scheme 2:



The structure of the original methyl 2-(2-naphthyloxy)vinyl ketone is not in doubt, since on reaction with p-nitrophenylhydrazine it yields 2-naphthol and 3-methyl-1-(p-nitrophenyl)pyrazole:

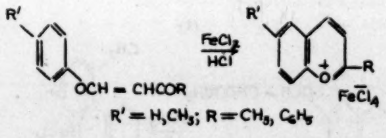


The result obtained in the reaction of the naphthoxyvinyl ketone with ferric chloride can be understood only on the assumption that, under the conditions of the reaction, there is initially a migration of the 3-oxo-1-alkenyl group from the oxygen to the carbon in the 1-position of the naphthalene nucleus, the intermediately formed 2-(2-hydroxy-1-naphthyl)vinyl methyl ketone than undergoing cyclization:



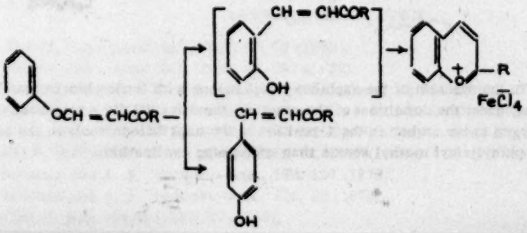
This rearrangement is reminiscent in its character of the well-known Fries rearrangement. This resemblance is in accord with the fact that, formally, 2-phenoxyvinyl ketones are so-called "vinylogs" of phenol esters, and from this point of view the reaction here described presents a new and interesting example of "vinylogy".

As further investigation has shown, the reaction is a fairly general one. Thus, when 2-(2-naphthyloxy)vinyl propyl ketone [1-(2-naphthyloxy)-1-hexen-3-one], which was synthesized by the general method for the preparation of phenoxyvinyl ketones already described [1], was treated with ferric chloride, a high yield of 3-propylnaphtho [2,1-b]pyrylium chloroferrate (III) was obtained. Under the same conditions, i.e., in presence of ferric chloride in a mixture of hydrochloric and acetic acids, phenoxyvinyl ketones of the benzene series are also converted into pyrylium salts. We verified this in the case of the rearrangements of methyl 2-phenyloxyvinyl ketone (4-phenoxy-3-buten-2-one) and methyl 2-p-tolyloxyvinyl ketone (4-p-tolyloxy-3-buten-2-one), and also of 2-phenoxyvinyl phenyl ketone (2-phenoxyacrylophenone), which was prepared by the action of phenol on 2-chlorovinyl phenyl ketone (2-chloroacrylophenone):

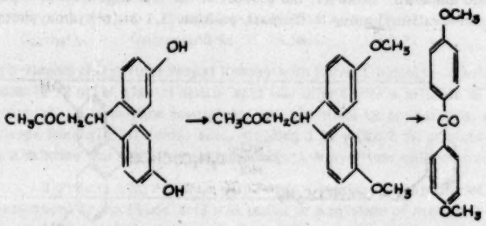


The benzopyrylium chloroferrates obtained in this way were found to be identical with disubstituted benzopyrylium salts obtained by another method, the structures of which are beyond doubt. In this case also, therefore, the reaction of phenoxyvinyl ketones with ferric chloride is accompanied by preliminary migration of the 3-oxo-1-alkenyl group into the aromatic nucleus.

We have further found that the yields of the pyrylium salts obtained by the rearrangement of methyl 2-(2-naphthyloxy)vinyl ketone and methyl 2-p-tolyloxyvinyl ketone are fairly high (94% and 58% respectively), whereas treatment of methyl 2-phenoxyvinyl ketone and 2-phenoxyvinyl phenyl ketone with ferric chloride gave only low yields (11.8% and 10%) of pyrylium salts. It is known that in the Fries rearrangement the acyl group may migrate either to the ortho or to the para position. It will be clear that, for the 3-oxo-1-alkenyl group also, migration both to the ortho and to the para position is possible. It is to be expected, therefore, that for methyl 2-(2-naphthyloxy)vinyl ketone and methyl 2-p-tolyloxyvinyl ketone, which have no free para positions, the only possibility is the formation of the ortho isomer, which will cyclize to a pyrylium salt, which is actually obtained in fairly high yield in these cases. On the other hand, in the case of methyl 2-phenoxyvinyl ketone and 2-phenoxyvinyl phenyl ketone, the formation of an ortho isomer is only one of the two possible directions that the reaction can take, and the yield of pyrylium salt is, therefore, less:

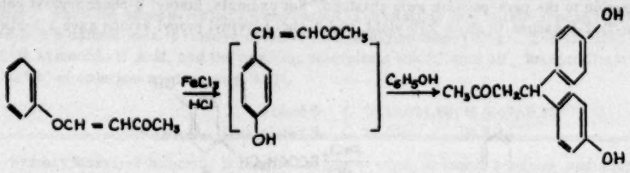


If this hypothesis is correct, then in the reaction of the two last compounds with ferric chloride we may expect the formation of the corresponding para-substituted styryl ketones. Actually, when methyl 2-phenoxyvinyl ketone reacted with ferric chloride, the reaction mixture yielded not only the pyrylium salt, but also a crystalline substance of m.p. 187°, which had the properties of a phenol. This compound, however, gave no reaction for a double bond and its melting point did not agree with that of 4-(p-hydroxyphenyl)-3-buten-2-one [3]. We established that this substance was the product of the further reaction of 4-(p-hydroxyphenyl)-3-buten-2-one under the conditions employed, and was 4,4-bis(p-hydroxyphenyl)-2-butanone. The structure of this substance was proved by methylation with dimethyl sulfate or methyl iodide and subsequent oxidation of the resulting dimethyl ether with permanganate, which yielded 4,4'-dimethoxybenzophenone:

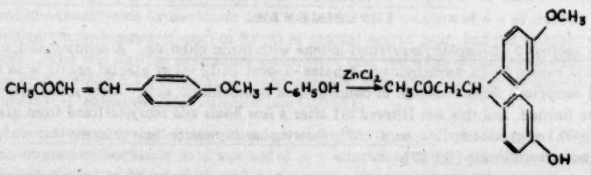


In the methylation, the monomethyl ether [4-(p-hydroxyphenyl)-4-(p-methoxyphenyl)-2-butanone] was isolated also.

The explanation of the formation of 4,4-bis-(p-hydroxyphenyl)-2-butanone when 2-chlorovinyl phenyl ketone is treated with ferric chloride must be that the 4-(p-hydroxyphenyl)3-buten-2-one formed unites with a further molecule of phenol, which is constantly present in the reaction mixture owing to the partial splitting of the phenoxyvinyl ketone in an acid medium:



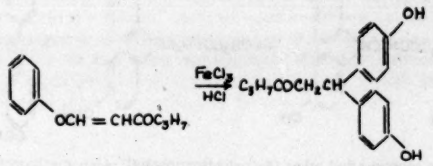
This hypothesis, which was based on known analogies from the literature [4, 5] was further confirmed by direct experiment. It was found that 4-(p-methoxyphenyl)-3-buten-2-one unites with one molecule of phenol in presence of zinc chloride, forming 4-(p-hydroxyphenyl)-4-(p-methoxyphenyl)-2-butanone, identical with the substance obtained by the methylation of 4,4-bis-(p-hydroxyphenyl)-3-buten-2-one:



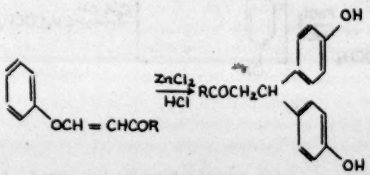
At the same time this confirmed the possibility of the addition of a molecule of phenol at the double bond of an α,β-unsaturated ketone in presence of such a mild agent as zinc chloride.

In the rearrangement of methyl 2-phenoxyvinyl ketone, therefore, we have succeeded in isolating not only the pyrylium salt formed as a result of the migration of the 3-oxo-1-alkenyl group to the ortho-position of the aromatic nucleus, but also a substance corresponding to migration to the para-position. A compound of the same type, 3,3-bis(p-hydroxyphenyl)propiophenone, was isolated together with the corresponding pyrylium salt in the rearrangement of 2-phenoxyvinyl phenyl ketone.

In the rearrangement of 2-phenoxyvinyl propyl ketone (1-phenoxy-1-hexen-3-one) in presence of ferric chloride, it was not found possible to isolate a pyrylium salt, owing to the extremely low stability of 2-alkyl-1-benzopyrylium salts containing the higher radicals. It is known, for example, that in an attempt to synthesize 2-ethyl-1-benzopyrylium chloroferrante (III) Decker [6] isolated a substance that decomposed completely in two hours, as a result of which he was unable ot obtain it in an analytically pure form. 2-Alkyl-1-benzopyrylium salts having heavier radicals are unknown. However, the product of the rearrangement of 2-phenoxyvinyl propyl ketone with migration of the 3-oxo-1-alkenyl group to the para-position [1,1-bis(p-hydroxyphenyl-3-hexanone)]was isolated:



The similarity between this rearrangement and the Fried rearrangement is further confirmed by the fact that ferric chloride is not the only agent promoting the reaction. It was found that, when phenoxyvinyl ketones having a free para-position in the aromatic nucleus were treated with zinc chloride in hydrochloric acid, products formed by migration to the para-position were obtained. For example, methyl 2-phenoxyvinyl ketone gave 4,4-bis (p-hydroxyphenyl)-2-butanone in about 20% yield, and 2-phenoxyvinyl propyl ketone gave 1,1-bis(p-hydroxyphenyl)-3-hexanone:



$R = CH_3, C_3H_7$

It should be emphasized, however, that the rearrangement of phenoxyvinyl ketones occurs only in aqueous hydrochloric acid and cannot be effected at all in inert solvents, such as are normally used for the Fries rearrangement.

EXPERIMENTAL

1. Reaction of methyl 2-(2-naphthyloxy)vinyl ketone with ferric chloride. A solution of 1.0 g of methyl 2-(2-naphthyloxy)vinyl ketone [4-(2-naphthyloxy)-3-buten-2-one] in 12 ml of glacial acetic acid was mixed with a solution of 5.0 g of anhydrous ferric chloride in concentrated hydrochloric acid. After a few minutes a yellow crystalline precipitate formed, and this was filtered off after a few hours and recrystallized from glacial acetic acid, yielding 1.7 g (90%) of green needles, m.p. 152°, showing no depression in a mixture test with 3-methyl-naphtho[2,1-b]pyrylium chlofoferrate (III) [2].

2. Reaction of methyl 2-(2-naphthyloxy)vinyl ketone with p-nitrophenylhydrazine. A solution of 0.27 g of methyl 2-(2-naphthyloxy)vinyl ketone and 0.2 g of p-nitrophenylhydrazine in 10 ml of glacial acetic acid was heated to the boil and then set aside for one day at room temperature. The precipitated crystals were filtered off and recrystallized from glacial acetic acid, yielding 0.25 g (89%) of brown needles, m.p. 165-166°, showing no

depression in a mixture test with 3-methyl-1-(p-nitrophenyl)pyrazole. To the filtrate 30 ml of water and 20 ml of 20% caustic soda solution were added, and the solution was filtered and acidified with 20% sulfuric acid. The resulting precipitate was filtered off and recrystallized from aqueous alcohol, yielding 0.17 g (85%) of colorless crystals, m.p. 120°, showing no depression in a mixture test with 2-naphthol.

3. Preparation of 2-(2-naphthyloxy)vinyl propyl ketone. To a vigorously stirred solution of 16.0 g of 2-naphthol in 50 ml of 10% caustic soda, 14.0 g of 2-chlorovinyl propyl ketone (1-chloro-1-hexen-3-one) was added dropwise; the reaction mixture was stirred for five hours and then set aside overnight. Water (250 ml) was then added, and the mixture was extracted with ether. The extract was dried over sodium sulfate, the solvent was distilled off, and the residue was vacuum-distilled, the fraction of b.p. 182-186° (4 mm) being collected (11.0 g, i.e., 51.3%). After redistillation the 2-(2-naphthyloxy)vinyl propyl ketone [1-(2-naphthyloxy)-1-hexen-3-one] was obtained as a yellowish oil, b.p. 184-186° (4 mm), n_D^{20} 1.6038.

Found %: C 79.78; 79.94; H 7.02; 6.94
$C_{18}H_{18}O_2$. Calculated %: C 79.98; H 6.71.

4. Reaction of 2-(2-Naphthyloxy)vinyl Propyl Ketone with Ferric Chloride. A solution of 1.0 g of 2-(2-naphthyloxy)vinyl propyl ketone in 12 ml of glacial acetic acid was mixed with a solution of 5.0 g of ferric chloride in concentrated hydrochloric acid. A crystalline precipitate quickly made its appearance, and after four hours it was filtered off and recrystallized from glacial acetic acid, yielding 1.52 g (85.7 %) of light-green crystals, m.p. 124°, showing no depression in a mixture test with 3-propylnaphtho[2,1-b]pyrylium chloroferrate (III).

5. Reaction of Methyl 2-Phenoxyvinyl Ketone with Ferric Chloride. A solution of 40 g of anhydrous ferric chloride in 60 ml of concentrated hydrochloric acid was added to a solution of methyl 2-phenoxyvinyl ketone (4-phenoxy-3-buten-2-one) in 80 ml of glacial acetic acid. The reaction mixture immediately became crimson in color, and after a few hours a red crystalline precipitate formed and was filtered off. Recrystallization from glacial acetic acid yielded 5.0 g (11.8%) of crimson needles, m.p. 125°, showing no depression in a mixture test with 2-methyl-1-benzopyrylium chloroferrate (III)[2]. To the filtrate from the separation of the 2-methyl-1-benzopyrylium chloroferrate (III) an equal volume of ether was added. The solution was repeatedly washed with water to remove ferric chloride, the process being continued until the aqueous layer ceased to become colored. The ether layer was then separated, and the ether was distilled off; the resinous residue was repeatedly extracted with boiling water. When the aqueous extracts were cooled, a crystalline precipitate appeared, and was filtered off and dissolved in 5% caustic soda to remove undissolved triacetylbenzene (0.2 g). The alkaline filtrate was acidified with 20% hydrochloric acid, and the resulting precipitate was filtered off. Recrystallization from water yielded 3.1 g (19.7%) of colorless needles, m.p. 187°.

Found %: C 75.10; 74.98; H 6.47; 6.29
$C_{16}H_{16}O_3$. Calculated %: C 75.00; H 6.25

4,4-Bis(p-hydroxyphenyl)-2-butanone is readily soluble in ether, acetone, benzene, and aqueous alkalis; it does not decolorize permanganate solution or bromine water. With prolonged keeping it gradually darkens.

6. Reaction of Methyl 2-Phenoxyvinyl Ketone with Zinc Chloride. A solution of 15 g of anhydrous zinc chloride in 30 ml of concentrated hydrochloric acid was added to a solution of 15.0 g of methyl 2-phenoxyvinyl ketone in 60 ml of glacial acetic acid. There was no change in outward appearance, and only after two days did the reaction mixture acquire a red color. The solution was filtered, diluted with ether, and treated further as described in the preceding experiment. The product was 1.7 g (29.6%) of 4,4-bis(p-hydroxyphenyl)-2-butanone, m.p. 187° showing no depression in a mixture test with the substance obtained in the preceding experiment.

7. Reaction of Methyl 2-p-Tolyloxyvinyl Ketone with Ferric Chloride. A solution of 10.0 g of ferric chloride in 15 ml of concentrated hydrochloric acid was added to a solution of 5 g of methyl 2-p-tolyloxyvinyl ketone (4-p-tolyloxy-3-buten-2-one) in 30 ml of glacial acetic acid, and the mixture was set aside at room temperature. After one day the crystalline precipitate that had formed was filtered off. Crystallization of glacial acetic acid yielded 5.7 g (56.4%) of violet crystals, m.p. 105°, showing no depression in a mixture test with 2,6-dimethyl-1-benzopyrylium chloroferrate (III) [7].

8. Reaction of 2-Phenoxyvinyl Propyl Ketone with Ferric Chloride. A solution of 15 g of ferric chloride in 22 ml of concentrated hydrochloric acid was added to a solution of 8.0 g of 2-phenoxyvinyl propyl ketone (1-phenoxy-1-hexen-3-one) in 25 ml of glacial acetic acid. The reaction mixture slowly became red, but no precipitate of a pyrylium salt formed. After one day the solution was filtered, diluted with ether, and treated

further as described for Expt. No. 5. Recrystallization of the product from water yielded 1.7 g (28%) of 1,1-bis (p-hydroxyphenyl)-3-hexanone in the form of colorless needles.

Found %: C 76.02; 75.94; H 6.94; 7.09
$C_{18}H_{20}O_3$. Calculated %: C 76.06; H 7.04

1,1-Bis(p-hydroxyphenyl)-3-hexanone is soluble in ether, benzene, alcohol, and aqueous alkalis; it does not decolorize permanganate solution or bromine water; with keeping it gradually darkens.

9. Preparation of 2-Phenoxyvinyl Phenyl Ketone. To a vigorously stirred solution of 10.0 g of phenol in 60 ml of 15% caustic soda 15.0 g of 2-chlorovinyl phenyl ketone (2-chloroacrylophenone) [7] was added dropwise. The reaction mixture was stirred for twelve hours at room temperature, and the oil that separated was extracted with ether. The extract was washed several times with 10% caustic soda and with water, and then dried over sodium sulfate. The solvent was distilled off, and the residue was vacuum-distilled, the fraction of b.p. 172-183° (4.5 mm) being collected; it crystallized in the receiver. Recrystallization from petroleum ether yielded 8.5 g (42.5%) of 2-phenoxyvinyl phenyl ketone (2-phenoxyacrylophenone) in the form of colorless crystals, m.p. 49-50° (the literature [8] gives 49.5-50°).

Found %: C 80.59; 80.33; H 5.44; 5.37
$C_{15}H_{12}O_2$. Calculated %: C 80.39; H 5.40

2-Phenoxyvinyl phenyl ketone is of good solubility in the usual organic solvents (poor in petroleum ether). It gradually darkens with keeping.

10. Reaction of 2-Phenoxyvinyl Phenyl Ketone with Ferric Chloride. A solution of 20 g of ferric chloride in 30 ml of concentrated hydrochloric acid was added to a solution of 5.5 g of 2-phenoxyvinyl phenyl ketone in 25 ml of glacial acetic acid. After three hours a crystalline precipitate formed. It was filtered off, washed on the filter with absolute ether, and recrystallized from glacial acetic acid, yielding 0.98 g (10%) of golden scales, m.p. 138°, showing no depression in a mixture test with flavylium chloroferrate (III) [7]. The filtrate from the separation of the flavylium chloroferrate was diluted with ether and repeatedly washed with water until the aqueous layer ceased to be colored. The ether layer was then extracted with 5% caustic soda and the alkaline extract was acidified. Recrystallization of the resulting resinous precipitate from alcohol yielded 0.7 g (20.5%) of colorless crystals, m.p. 198-199°.

Found %: C 79.05; 79.08; H 6.02; 5.91
$C_{21}H_{18}O_3$. Calculated %: C 79.20; H 5.70

3,3-Bis(p-hydroxyphenyl)propiophenone is soluble in alcohol, ether, boiling water, and aqueous solutions of alkalis.

11. Methylation of 4,4-Bis(p-hydroxyphenyl)-2-butanone. 4,4-Bis(p-hydroxyphenyl)-2-butanone (0.6 g) and methyl iodide (0.8 g) were added to a solution of sodium methoxide prepared by dissolving 1.5 g of sodium in 50 ml of absolute methanol, and the reaction mixture was heated for 30 hours in a water bath. The methanol was distilled off, and 50 ml of 5% caustic soda was added to the residue. The extract was dried over sodium sulfate, and the ether was distilled off. After a few days the residue crystallized out completely. Recrystallization from petroleum ether yielded 0.4 g (60.6%) of colorless needles of 4,4-bis(p-methoxyphenyl)-2-butanone, m.p. 41-42°.

Found %: C 76.00; H 7.01
$C_{18}H_{20}O_3$. Calculated %: C 76.05; H 7.09

4,4-Bis(p-methoxyphenyl)-2-butanone is of good solubility in the usual organic solvents (poor in petroleum ether).

The semicarbazone was prepared in the usual way. After recrystallization from aqueous alcohol it was obtained as colorless crystals, m.p. 156°.

Found %: N 12.66; 12.73
$C_{19}H_{23}O_3N_3$. Calculated %: N 12.76

Isolation of 4-(p-hydroxyphenyl)-4-(p-methoxyphenyl)-2-butanone. To the alkaline solution obtained after the extraction of the dimethyl ether of 4,4-bis(p-hydroxyphenyl)-2-butanone, 40 ml of 20% caustic soda was added, when the sodium salt of 4-(p-hydroxyphenyl)-4-(p-methoxyphenyl)-2-butanone, which is sparingly soluble in alkali, separated from the solution. The precipitate was filtered off, dissolved in water, and again precipitated

by addition of alkali. This operation of purification from the dimethyl derivative was repeated four or five times, and the sodium salt of the monomethyl derivative was then dissolved in water and the solution acidified with 20% hydrochloric acid; the crystals that separated were filtered off. Recrystallization from water yielded 0.12 g (19%) of colorless needles, m.p. 121-122°.

Found %: C 75.48; 75.46; H 6.94; 6.77
$C_{17}H_{18}O_3$. Calculated %: C 75.53; H 6.71

The needles dissolve readily in ether and alcohol; less readily in hot water.

When 4,4-bis(p-hydroxyphenyl)-2-butanone was methylated under the usual conditions with dimethyl sulfate, the dimethyl derivative was obtained in 65.2% yield, and the monomethyl derivative in 17% yield.

12. Oxidation of 4,4-Bis(p-methoxyphenyl)-2-butanone. To a suspension of 1.5 g of the substance in 50 ml of a 5% solution of sodium carbonate, 4.4 g of finely ground potassium permanganate was added, and the reaction mixture was boiled for three hours. The mixture was cooled, and the precipitate of manganese dioxide and 4,4'-dimethoxybenzophenone was filtered off and washed carefully on the filter, first with 10% sodium carbonate solution, and then with a saturated solution of oxalic acid. The undissolved residue was recrystallized from alcohol, and yielded colorless crystals, m.p. 142-143°, showing no depression in a mixture test with 4,4'-dimethoxybenzophenone.

13. Reaction of 4-(p-Methoxyphenyl)-3-buten-2-one with Phenol. Phenol (0.5 g) and a solution of 4.0 g of anhydrous zinc chloride in 5 ml of concentrated hydrochloric acid were added to a solution of 0.7 g of 4-(p-methoxyphenyl)-3-buten-2-one in 20 ml of glacial acetic acid, and the reaction mixture was set aside for two days at room temperature. The mixture was then diluted with 150 ml of ether and washed with water until the washings ceased to be colored. The ether layer was extracted with a 3% solution of caustic soda, and the alkaline extract was acidified with 20% hydrochloric acid. The precipitated crystals of 4-(p-hydroxyphenyl)-4-(p-methoxyphenyl)-2-butanone (0.7 g, i.e. 69%) were filtered off. Recrystallization from water yielded colorless crystals, m.p. 121-122°, showing no depression in a mixture test with the substance obtained in Expt. No. 11.

SUMMARY

1. It has been shown that in the reaction of 2-phenoxy- and 2-(2-naphthyloxy)-vinyl ketones with ferric chloride in a mixture of acetic and concentrated hydrochloric acids, a rearrangement associated with the migration of the 3-oxo-1-alkenyl group to the ortho- and para-positions in the aromatic nucleus takes place.

2. 2-(2-Naphthyloxy)- and 2-phenoxy-vinyl ketones having a para-substituent in the aromatic nucleus give α-substituted naphtho- and benzo-pyrylium salts when treated with ferric chloride.

3. 2-Phenoxyvinyl ketones having no para-substituent in the aromatic nucleus give mixtures of the benzopyrylium salt and the alkyl 2,2-bis(p-hydroxyphenyl) ethyl ketone when treated with ferric chloride.

4. It has been shown that zinc chloride in hydrochloric acid also promotes the rearrangement of phenoxyvinyl ketones, resulting in the formation of only alkyl 2,2-bis(p-hydroxyphenyl) ethyl ketones.

5. It has been shown that, in presence of zinc chloride, 4-(p-methoxyphenyl)-3-buten-2-one unites at its double bond with a molecule of phenol.

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Received July 8, 1953

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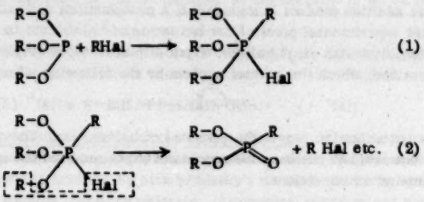
EFFECT OF THE SIZE AND STRUCTURE OF RADICALS PRESENT IN PHOSPHORUS ESTERS ON THE RATE OF ISOMERIZATION OF THESE SUBSTANCES*

A. E. Arbuzov and L. V. Nesterov

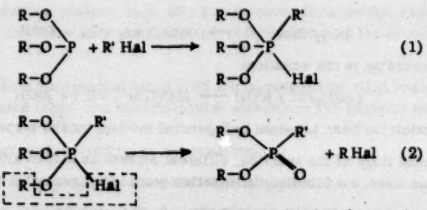
In 1905, while studying the reaction of trialkyl phosphites with alkyl halides, one of us [1] discovered the isomerization of trialkyl phosphites into esters of alkylphosphonic acids. Further study of this reaction showed that it is catalytic, since the amount of alkyl halide can be reduced to a very low value without affecting the yield. Such is the process that occurs when the alkyl of the alkyl halide is identical with the alkyls of the phosphorous ester.

When the trialkyl phosphite was treated with an equimolecular amount of an alkyl halide in which the alkyl was not identical with the alkyls of the phosphorous ester, a reaction was found to occur which has since been given the name of the "Arbuzov rearrangement". At the same time a mechanism was proposed for these transformations: the isomerization and rearrangement reactions proceed in two stages. The first stage consists in the addition of alkyl halide to trialkyl phosphite. In the case of the isomerization reaction the addition product is extremely unstable, and the second stage, elimination of alkyl halide in which an ester alkyl is removed, sets in at the same temperature. When the trialkyl phosphite is treated with an alkyl halide containing an alkyl of different molecular weight or structure, then, as in the case of isomerization, in the first stage an addition product is formed, and in the second stage there occurs the elimination of the halide of the alkyl originally present in the trialkyl phosphite. All of these reactions are shown in the schemes below:

Isomerization of phosphorous esters:

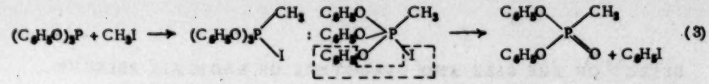


"Arbuzov rearrangement":



In the case of phosphorous esters in which R is an aliphatic radical, it has not been found possible to isolate, or even to detect, the intermediate addition product, but in the case of esters in which R is aromatic, the addition product is sometimes stable and may be isolated in the analytically pure state. These addition products are crystalline products, and they were first obtained by chemists of the Michaelis school [2]. With the aid of one of these, the product of the addition of methyl iodide to triphenyl phosphite, direct confirmation was obtained of the above scheme for the mechanism of the rearrangement. In this case the two stages can be effected separately:

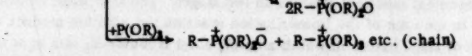
* A study of the mechanism of the Arbuzov rearrangement.



(3)

The addition (the first stage) goes at 100°, and the decomposition (the second stage) at a much higher temperature. This is the only case that has been described of the separate realization of the two stages of the Arbuzov rearrangement. An attempt to decompose the analogous addition products formed by methyl iodide with the phenyl esters of phenylphosphonous and diphenylphosphinous acids [3] was not successful.

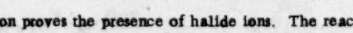
In spite of the fact that in many cases it has not been found possible to isolate the intermediate addition products, there can be little doubt that they are formed. This scheme has been confirmed by all of the great variety of syntheses (more than 300) carried out by Soviet and foreign chemists. By means of the Arbuzov rearrangement compounds have been obtained containing the linkages phosphorus–carbon, phosphorus–silicon, phosphorus–tin, phosphorus–phosphorus, and phosphorus–arsenic. The above scheme of the mechanism of the Arbuzov rearrangement in its general form is accepted by the majority of chemists. Only Rumpf [4] regards the rearrangement (more accurately, its special case: isomerization) as a chain reaction, for which he proposes the following scheme:



(4)

Rumpf, however, gives no experimental confirmation of his scheme, but refers to the possibility of obtaining derivatives of methylphosphonic acid by heating pure dimethyl phosphite.

Although the general scheme of the rearrangement reaction is almost universally accepted, views on particular details are at variance. The first stage, i.e., addition, is regarded by all authors as analogous to the well-known Menshutkin reaction [5], which, according to Menshutkin's own investigations, is a second-order reaction. The interemediate addition product is regarded as a phosphonium derivative $[(RO)_3PR']^+Hal^-$. Gerrard and Green [6] bring forward experimental proof of the formation of halide ions in the reaction medium during the reaction of trialkyl phosphites with alkyl halides. Optically active 1-methylheptyl halide present in such a mixture, is gradually racemized, which the authors explain by the following scheme of ion exchange:



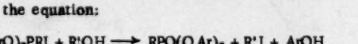
(5)

and they consider that the racemization proves the presence of halide ions. The reaction was carried out at about 100°. The authors, however, do not describe any blank experiment on the racemization of 1-methylheptyl halide under the same temperature conditions.

The crystalline addition products are of low stability [1, 2, 3], and react with water [2] according to the equation:

(6)

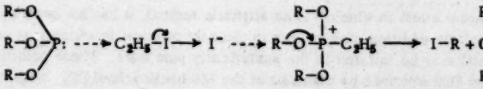
and with alcohols [1, 3] according to the equation:



(7)

Incidentally, the last reaction has been proposed as a general method for the preparation of the alkyl halides R'I •.

As regards the second stage of the reaction, different authors treat it in different ways. Gerrard and Green [6] consider that the second stage is a bimolecular reaction proceeding according to the scheme:



(8)

If R is the radical of an optically active alcohol, then after the reaction the radical of the alkyl halide IR acquires the reverse configuration, thus confirming the bimolecular mechanism of the reaction.

• The British authors Landauer and Rydon ascribe the priority of the discovery of the reaction in Equation 7 to themselves, although it was described by one of us [1] 45 years previously.

Pudovik [7] supposes that the second stage is bimolecular only when the radical R of the phosphorous ester $P(OR)_3$ is primary. When the radical is secondary, the reaction may be either uni- or bi-molecular, and when it is tertiary, the reaction may be only unimolecular. For primary radicals, therefore, Pudovik proposes a scheme completely analogous to Gerrard's scheme. In the case of secondary radicals, first of all an unsaturated carbonium ion is eliminated (by a unimolecular mechanism), and in this oscillation of the double bond occurs, so that when it unites with a halide ion a mixture of almost equal amounts of isomeric alkyl halides is obtained. All these conclusions, however, are based on indirect evidence; no observations have been made of the kinetics of the second stage of the rearrangement of aliphatic phosphorous esters, and it does not appear to be possible to carry out such observations.

Observations on the kinetics of the Arbuzov rearrangement have been made [8, 9, 10] only in a few special cases of isomerization. Observations on the general case of rearrangement have been made only once [11], and these cannot pretend to high accuracy. The first investigations of this sort were carried out in 1914 [8]. It was established that the isomerization was not a first-order reaction, but was similar to catalytic (enzymic) processes. The isomerization curves had a characteristic S bend, i.e., in the first stages of the reaction it was accelerated, as if proceeding contrary to the mass-action law. The effect of self-heating on the process was excluded by careful thermostatic control. The question of the autocatalytic effect of the isomerization product was answered in the negative [8], since a mixture of the pure phosphorous ester and its isomer underwent no change when heated for a long time at 155°.

Zawidski and Staronka [9], however, gave a different answer to the question of the autocatalytic effect of the isomerization product. They supposed that the isomerization product speeds up the reaction, but only in presence of alkyl halide. They considered, therefore, that in the case of isomerization "complex" autocatalysis is observed; for the rate of such a reaction they proposed the equation:

$$\frac{dx}{dt} = k(1+nx)(1-x), \qquad (9)$$

(x is the relative concentration of the reaction product, and n is a constant in a given experiment). When the reaction is carried out in a solvent, the "conjugation" between the alkyl halide and the isomerization product is broken, and the accelerating effect of the latter does not appear. Staronka [10] has proposed another interpretation for Equation 9, the basis of this being the variation of the composition of the medium in which the reaction occurs.

In the present investigation we have carried out isomerization experiments on some new mixed phosphorous esters, experiments on the addition of alkyl iodides to triphenyl phosphite, and experiments on the thermal decomposition of the addition products; the rates of all of these reactions have been studied.

EXPERIMENTAL

Preparation of Mixed Phosphorous Esters, and their Isomerization. Mixed aliphatic-aromatic phosphorous esters were studied: they were prepared from phenyl phosphorodichloridite and diphenyl phosphorochloridite and the corresponding alcohols in an ether medium by Milobendzsky's method. Dimethylaniline and, in one case, pyridine were used as agents for binding hydrogen chloride. Altogether, seven mixed phosphorous esters were synthesized. They are all colorless, fairly mobile liquids, which react with cuprous halides with evolution of heat. A crystalline cuprous chloride addition product, m.p. 69°, was prepared from methyl diphenyl phosphite; it was not found possible to crystallize the other addition products. The properties of the mixed phosphorous esters are given in Table 1 (Nos. 1-7).

The reactions of all of these phosphorous esters with the corresponding alkyl iodide were studied. The reactions were carried out in sealed tubes, and equimolecular amounts of the reagents were taken. Smooth isomerization occurred only in the case of dimethyl phenyl, methyl diphenyl, diethyl phenyl, and ethyl diphenyl phosphites, and the reactions then went according to the equations:

$$(C_6H_5O)_2POR + RI \longrightarrow RPO(OC_6H_5)_2 + RI$$

$$C_6H_5OP(OR)_2 + RI \longrightarrow RPO(OR)(OC_6H_5) + RI.$$

The properties of the resulting phenyl and mixed esters of alkylphosphonic acids are given in Table 1 (Nos.8-11). All of these esters are liquids of higher viscosity than the isomeric phosphorous esters. Product No. 8 is soluble in water in all proportions; the remainder are not appreciably soluble in water.

The phosphorous esters Nos. 3, 4, and 5 do not appear to react with the corresponding alkyl iodides below 200°; above 200° decomposition sets in. We, therefore, prepared the phenyl esters of the higher alkylphosphonic acids by another method.

TABLE 1

No.	Ester	Temperature(°C) (p in mm Hg)	d_4^{20}	n_D^{20}	MR found	MR calc'd	Yield (%)
1	$(C_6H_5O)_2POCH_3$	165.5-166.5 (12)	1.1644 (23°)	1.5528 (23°)	68.18	68.10	56
2	$(C_6H_5O)_2POC_2H_5$	182 - 183 (17.5)	1.1372 (21°)	1.5475 (21°)	73.18	72.72	60.5
3	$(C_6H_5O)_2PO$ i-C_3H_7	170 - 171 (10)	1.1073	1.5394	78.20	77.33	58
4	$(C_6H_5O)_2PO$ p-C_4H_9	187 - 187.5 (9.5)	1.0967 (21°)	1.5370 (21°)	82.66	81.95	52
5	$(C_6H_5O)_2PO$ i-C_4H_9	180.5-181 (9)	1.0952 (21°)	1.5358 (21°)	82.62	81.95	68
6	$C_6H_5OP(OCH_3)_2$	96 - 97 (9)	1.1267	1.5053	49.03	48.61	50.6
7	$C_6H_5OP(OC_2H_5)_2$	113 (11)	1.0659	1.4933	58.44	57.85	35.3
8	$CH_3PO(OCH_3)(OC_6H_5)$	135 - 136 (11)	1.1914	1.5054	46.37	46.41	98.5
9	$C_2H_5PO(OC_2H_5)(OC_6H_5)$	142.5-143.5 (12.5)	1.1197	1.4922	55.52	55.65	84
10	$CH_3PO(OC_6H_5)_2$	192 - 192.5 (9)	1.2058	1.5518	65.75	65.90	88.3
11	$C_2H_5PO(OC_6H_5)_2$	202 (13)	1.1799	1.5451	70.29	70.52	80
12	i-$C_3H_7PO(OC_6H_5)_2$	198 - 200 (10.5)	1.1497	1.5383	75.20	75.14	33.7
13	p-$C_4H_9PO(OC_6H_5)_2$	205 - 207.5 (11)	1.1293	1.5339	79.89	79.76	52
14	i-$C_4H_9PO(OC_6H_5)_2$	190 - 192 (11.5)					35
15	$C_6H_5CH_2PO(OC_6H_5)_2$		M.p.66°				76
			M.p.104°				

TABLE 2

No.	Substance	Temperature (°C) of prep.	Temperature (°C) of melting	Amount of I (%) found	Amount of I (%) calc'd	Yield (%)
16	$(C_6H_5O)_2P(CH_2C_6H_5)I$	120	112-114	24.23	24.02	Quantitative
17	$(C_6H_5O)_2P(CH_3)I$	130	130	28.31; 28.32	28.06	Quantitative
18	$(C_6H_5O)_2P(C_2H_5)I$	130	89-91	27.43; 27.31	27.16	Quantitative
19	$(C_6H_5O)_2P(i\text{-}C_3H_7)I$	160	110	26.58; 26.57	26.43	12.1
20	$(C_6H_5O)_2P(p\text{-}C_4H_9)I$	170		Not isolated in pure state		
21	$(C_6H_5O)_2P(i\text{-}C_4H_9)I$	150	157-157.5	26.61; 26.67; 26.87	25.68	

Preparation of the Addition Products of Alkyl Iodides with Triphenyl Phosphite. The addition products of alkyl iodides with triphenyl phosphite were prepared by Michaelis' method. An equimolecular mixture of triphenyl phosphite and alkyl iodide was sealed in a tube, which was then heated at a definite temperature (Table 2: temperature of preparation) until the reduction in volume stopped. With one exception, all of the addition products were obtained in the crystalline state and were recrystallized from a mixture of dichloroethane and ether; their properties are given in Table 2.

It was not found possible to purify the isobutyl iodide addition product (No. 21) sufficiently to obtain satisfactory analytical figures, although the product was purified by means of four careful recrystallizations, and the melting point of the crystals did not change in the last two of these. We did not succeed in elucidating the cause of the nonagreement of the analyses.

Reaction of Alkyltriphenoxyphosphonium Iodides with Alcohol. The phenyl esters of higher alkylphosphonic acids, which we were unable to prepare by isomerization of the corresponding mixed phosphorous esters, were prepared by the reaction of Equation 7. The properties of the resulting esters are given in Table 1 (Nos. 12-15).

Thermal Decomposition of Alkyltriphenoxyphosphonium Iodides. All of the alkyltriphenoxyphosphonium iodides that we prepared were subjected to heating in sealed tubes at 210-220°. Decomposition then occurred in accordance with the scheme for the second stage of the Arbuzov rearrangement. Decomposition was accompanied by resinification processes, particularly in the case of the higher homologs. An appreciable amount of iodine separated, and this greatly complicated the purification process. We removed iodine by a new method, namely, by means of trimethyl phosphite. The results of the experiments are given in Table 3.

TABLE 3

Substance	Decomposition temperature, °C (time in hours)	Yield (%)		B.p. of $RPO(OPh)_2$ in °C (p in mm Hg)		n_D^{20} of $RPO(OPh)_2$	
		C_6H_5I	$RPO(OPh)_2$	of pure sub.	of sub. obtained	of pure substance	of sub. obtained
$(C_6H_5O)_3P^{+}(CH_3)\,I^{-}$	220 (20)	74	56	192-192.5 (9)	196-199 (12)	1.5518	1.5520
$(C_6H_5O)_3P^{+}(C_2H_5)\,I^{-}$	220 (20)	71	60	202 (13)	200-204 (12)	1.5451	1.5454
$(C_6H_5O)_3P^{+}(i\text{-}C_3H_7)\,I^{-}$	208 (15)	35	(50)	198-200 (10.5)	202-205 (12)	1.5383	1.5480
$(C_6H_5O)_3P^{+}(n\text{-}C_4H_9)\,I^{-}$	220 (15)	15	(51)	205-207.5 (11)	203-209 (10)	1.5339	1.5410
$(C_6H_5O)_3P^{+}(CH_2C_6H_5)\,I^{-}$	208 (20)	15	–	–	–	–	–
$(C_6H_5O)_3P^{+}(i\text{-}C_4H_9)\,I^{-}$	210 (15)	Only crystalline iodine isolated					

In the decomposition products of n-butyltriphenoxyphosphonium iodide, it was shown that not less than 75% of diphenyl n-butylphosphonate was present (isolated as crystalline n-butylphosphonic acid from the hydrolyzed high-boiling fraction). In the decomposition products of isopropyltriphenoxyphosphonium iodide, only iodobenzene was detected. The high-boiling fraction probably contained diphenyl isopropylphosphonate, but we did not succeed in isolating isopropylphosphonic acid from the hydrolysis products.

The formation and decomposition of alkyltriphenoxyphosphonium iodides provide confirmation of the scheme of the Arbuzov rearrangement proposed by its discoverer.

Study of the Kinetics of the Reaction. The procedure employed in the observations on the kinetics of the isomerization was based on the change in the volume of the reaction mixture and has been described in great detail by A. E. Arbuzov [8]. No essential modifications were introduced in our experiments. Equimolecular proportions of reactants were taken in the reaction mixtures. Each phosphorous ester isomerization reaction and reaction of addition of alkyl iodide to triphenyl phosphite was studied at two different temperatures. From the figures obtained the temperature coefficients of the reactions were calculated, and the results for all of the reactions were reduced to the same temperature.

Table 4 gives the main results of the isomerization experiments and Table 5 gives the results of the addition experiments.

TABLE 4

Original mixture	Temp. of expt. (°C)	Time (min) for a conversion of 25%	50%	75%	100%	Temp. coeff.	Time for 100 % conversion adjusted to 100° (hours)
$(C_6H_5O)_2POCH_3 + CH_3I$	80.3	108	200	315	790	1.94	3.6
	92	49	92	146	345		
$(C_6H_5O)_2POC_2H_5 + C_2H_5I$	110	6.25 hour	13.25 hour	21.67 hour	60 hour	1.96	117.5
	156	16.5	35	62.5	195		
$C_6H_5OP(OCH_3)_2 + CH_3I$	64.5	48	86	130	315	2.34	0.41
	72	28	45	64	180	(2.06)	
$C_6H_5OP(OC_2H_5)_2 + C_2H_5I$	110	66	133	222	507	2.10	17.7
	130	14	30	55	195		

TABLE 5

RI	Temp. of expt. (°C)	Time (hr) for addition of 25%	50%	75%	100%	Temp. coeff.	Time for 100% addition adjusted to 100° (hours)
$C_6H_5CH_2I$	110	0.484	0.833	1.25	3.75	1.88	8.52
	130	0.14	0.23	0.35	1.65		
CH_3I	110	0.63	1.33	2.53	10.75	1.97	19.4
	130	0.17	0.33	0.64	2.50		
C_2H_5I	110	18.0	38.5	70.0	–	2.10	510
	155	0.724	1.326	2.20	8.50		
i-C_3H_7I	176	3.75	7.1	10.35	21.0	(2)	4200
n-C_4H_9I	155	2.85	5.38	12.17	36.0	2.05	2120
	176	0.55	1.25	2.94	10.0		
i-C_4H_9	155	4.71	5.22	5.94	7.00	1.83	214
	176	1.26	1.52	1.69	2.33		

The isomerization curves that we obtained did not correspond to a reaction of the first order; neither could they be described by Equation 9 of Zawidski and Staronka. Since the addition of alkyl iodides to triphenyl phosphite is accompanied by various side reactions and resinifications, particularly in the case of the higher homologs, the reaction curves cannot, of course, characterize the processes correctly. However, in the majority of cases they were fairly close to first-order reaction curves.

The addition of isobutyl iodide to triphenyl phosphite calls for special comment, for it is about ten times as rapid as the addition of n-butyl iodide, and at the same time it has a considerable induction period. We intend to study this case in greater detail. The decomposition of alkyltriphenoxyphosphonium iodides was accompanied by increase in volume, which permitted us to follow the kinetics of the reactions by the same method as that used in the preceding experiments. The temperature of the experiments was 208°. The results are given in Table 6.

In order to determine the effect of the reaction product on the rate of isomerization, we carried out a number of experiments on the isomerization of dimethyl phenyl phosphite, and in these we added various amounts of methyl phenyl methylphosphonate to the original equimolecular mixture of methyl iodide and the phosphorous ester at the beginning of the experiment. All of the experiments were carried out at 64.5°. The composition of

of the original mixture was $C_6H_5OP(OCH_3)_2 + xCH_3PO(OCH_3)(OC_6H_5) + CH_3I$. The results are given in Table 7.

TABLE 6

Substance	Time (hr) for decomposition of			
	25%	50%	75%	100%
$(C_6H_5O)_3P^{+}(CH_2C_6H_5)\,I^-$	0.4	1.38	4.18	18.0
$(C_6H_5O)_3P^{+}(CH_3)\,I^-$	3.2	7.8	15.6	30
$(C_6H_5O)_3P^{+}(C_2H_5)\,I^-$	3.7	8.2	14.0	32
$(C_6H_5O)_3P^{+}(i\text{-}C_3H_7)\,I^-$	2.4	5.1	9.5	19
$(C_6H_5O)_3P^{+}(n\text{-}C_4H_9)\,I^-$	2.42	4.5	8.67	17.5

TABLE 7

x	Time (min) in which the percentage of the phosphorous ester that reacted was			
	25%	50%	75%	100%
0.000	48	86	130	315
0.200	39	71	110	240
0.500	34	67	107	230
1.000	32	62	105	240

Addition of the isomer to the original mixture, it will be seen, accelerates the reaction. The gradual acceleration of the reaction observed by various authors and by us is to be explained by the autocatalytic effect of the reaction product, which apparently acts as a solvent in which the rate of isomerization is appreciably greater than in the original mixture.

SUMMARY

1. Some new dialkyl phenyl and alkyl diphenyl phosphites have been synthesized.

2. In the series of alkyl diphenyl phosphites, only the methyl and ethyl esters isomerize smoothly. The higher homologs decompose when they react with the corresponding alkyl iodides.

3. A number of new addition products of alkyl iodides with triphenyl phosphite has been prepared.

4. The products of the addition of methyl, ethyl, and n-butyl iodides to triphenyl phosphite decompose at 210-220° according to the scheme of the second stage of the Arbuzov rearrangement.

5. By the action of alcohol on the products of the addition of benzyl, isopropyl, n-butyl, and isobutyl iodides to triphenyl phosphite, the diphenyl esters of the corresponding alkylphosphonic acids have been prepared; these reactions confirm the structures of the addition products.

6. The above facts (3, 4, and 5) show that the Arbuzov rearrangement occurs in two stages with the formation of an intermediate addition product.

7. It has been shown that the isomerization products of phosphorous esters are substances that accelerate the isomerization process. The isomerization reaction is therefore autocatalytic.

8. Isobutyl iodide adds to triphenyl phosphite considerably more rapidly than n-butyl iodide does. The addition reaction of isobutyl iodide, unlike those of the other alkyl iodides examined, has a long induction period.

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Received June 19, 1953

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ATOMIC REFRACTION OF PHOSPHORUS AND SULFUR IN PHOSPHOROTHIOLOTHIONIC ESTERS

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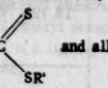
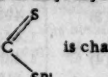
As is well known, the value of the atomic refraction of phosphorus in organic compounds is highly subject to constitutive effects: it depends on the valency state of the element and on the character of the bonds that it forms. Investigations on the atomic refraction of phosphorus have been carried out by Kovalevsky [1], Arbuzov [2], Jones, Davies, and Dyke [3], and others. In 1948 one of us [4] worked out the most probable values of the atomic refraction of phosphorus in certain types of organophosphorus compounds. Thus, for trialkyl phosphites the value determined (D line of sodium) was 7.04, for alkyl esters and other derivatives of phosphoric, phosphorochloridic, and phosphorodichloridic acids it was 3.76, and for derivatives of alkylphosphonic acids (esters and acid chlorides) it was 4.27. In the derivation of these constants, the generally accepted atomic refraction constants of Eisenlohr were used, the value assumed for chlorine attached to phosphorus being that found for chlorine in acid chlorides, namely 6.336 [5]; for the oxygen of the P=O group the value 2.211 was taken. The values so derived for the atomic refraction of phosphorus have been used since by many investigators [6], who have obtained good agreement between found and calculated values of the molecular refractions of organophosphorus compounds.

In the case of molecular refraction calculations on organic compounds containing sulfur and phosphorus, there is, as yet, an absence of reliable data on the atomic refraction of sulfur attached to phosphorus in the various types of these compounds. Jones, Davies, and Dyke [3] calculated the atomic refractions of sulfur in trimethyl phosphorothionate and trimethyl phosphorothiolate, and obtained the values 6.23 and 7.49 respectively. These values were calculated by the use of atomic constants for carbon, hydrogen, and oxygen that differed from Eisenlohr's constants, and the value 9.14 was used for the atomic refraction of phosphorus. Suitable recalculation of the results yields the values 9.68 for the sulfur of the P=S group and 8.12 for the sulfur of the P–S–R group. Although the first of these values has been confirmed by later results [7], the value of the atomic refraction of thiol sulfur in organophosphorus compounds continues to rest on the single example mentioned.

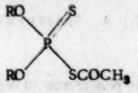
Molecular refraction calculations for organophosphorus compounds show that, when the above-cited atomic constants are used for phosphorus, the values of the atomic refractions of carbon, hydrogen, oxygen, and the halogens, and of the constitutive increments, remain the same as those established for the corresponding carbon compounds [4]. It is, therefore, of interest to determine whether the values of the atomic refraction of sulfur attached to phosphorus correspond to those of sulfur attached to carbon.

The atomic refraction of sulfur in carbon compounds has been the subject of numerous investigations. In a long paper by Boudet and Rambaud [8] there is a review of the available data on this question, and, on the basis of numerous examples, the values of the atomic refraction of sulfur (D line of sodium) are determined for various sulfur compounds. In particular, for the doubly bound sulfur of thiones the value 9.70 is obtained; in alkanethiols sulfur has the value 7.81, in dialkyl sulfides 8.00, and in alkyl aryl sulfide 9.20. The group S_2 in alkylxanthic esters  and alkanecarbodithioic esters  is characterized, according to their results, by an average group refraction of 18.78. According to Vogel [9], the refraction of sulfur in dialkyl sulfides is 7.92. In the case of alkylxanthic esters he uses a method of calculating group refractions that differs from that generally accepted. When the group refraction of S_2 is calculated in the usual way from his experimental results, the value obtained is 18.67, which is in good agreement with Boudet and Rambaud's results.

Having synthesized for the first time pure O,O-dialkyl S-hydrogen phosphorothiolothionates $(RO)_2PSSH$ [10], which are phosphorus analogs of xanthic acids, we determined the group refraction of the two sulfur atoms in these compounds*. It was found to be 18.82 ± 0.07, i.e., almost equal to the value 18.78 derived by

* There is a misprint in the paper cited [10] on page 729: The value of the atomic refraction of thiol sulfur is given at 9.34, instead of 9.06.

Boudet and Rambaud for the two sulfur atoms of the alkylxanthic esters and alkanecarbodithioic esters. With a view to making a more complete comparison of the atomic refractions of sulfur in derivatives of phosphorothiolothionic and alkylxanthic acids, we have synthesized, apart from the above-mentioned O,O-dialkyl S-hydrogen phosphorothiolothionates, some trialkyl phosphorothiolothionates $(RO)_2PS(SR)$ and some S-acyl derivatives of O,O-dialkyl S-hydrogen phosphorothiolothionates of two types (which will be named in this paper as O,O-dialkyl S-acyl (or S-alkoxycarbonyl) phosphorothiolothionates):



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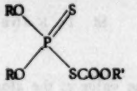
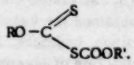


The results obtained are given in the table.

It was found that the average value of the group refraction of S_2 is 18.72 ± 0.07 in the trialkyl phosphorothiolothionates, and 19.77 ± 0.03 in the acyl derivatives.

As will be seen from the table, among compounds of a given type the refraction of the group S_2 retains a constant value, the departure from the mean value being small and not outside the usual errors of measurement. A comparison of the refractions of the group S_2 in trialkyl phosphorothiolothionates and alkylxanthic esters (18.72 and 18.78) shows that the group S_2 has the same refraction in combination with phosphorus and in combination with carbon. This again confirms the hypothesis referred to above concerning the equality of the atomic refractions of elements in combination with carbon and with phosphorus.

The S-acyl derivatives of O,O-dialkyl S-hydrogen phosphorothiolothionates are characterized by a higher value of the group refraction of the two sulfur atoms, namely 19.77. This value should be compared with the refraction of sulfur in the corresponding acyl derivatives of alkylxanthic acids:



Substances of this type are known. Thus, the ethyl derivative has d_4^{20} 1.180 and n_D^{20} 1.527 [11]. From these figures the refraction of the two sulfur atoms is found to be AR_{S_2} 19.53, which is near to the value 19.77, which we obtained for S-acyl derivatives of O,O-dialkyl S-hydrogen phosphorothiolothionates.

No.	Compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	Found MR_D	AR_{S_2}	Mean value of AR_{S_2}
1	$(CH_3O)_2PSSH$	62-68 (4.5)	1.5343	1.2888	38.16	18.58	
2	$(C_2H_5O)_2PSSH$	81.5-82.5 (5)	1.5070	1.1654	47.56	18.74	
3	$(C_3H_7O)_2PSSH$	85-86 (3)	1.4987	1.1040	56.96	18.91	18.82 ± 0.07
4	$(i\text{-}C_3H_7O)_2PSSH$	71-72 (3)	1.4918	1.0911	56.96	18.91	
5	$(i\text{-}C_4H_9O)_2PSSH$	93 (4)	1.4889	1.0558	66.23	18.94	
6	$(CH_3O)_2PS(SCH_3)$	101-101.5 (16.5)	1.5292	1.2415	42.79	18.59	
7	$(C_2H_5O)_2PS(SC_2H_5)$	115-115.5 (10)	1.5013	1.1168	56.56	18.50	
8	$(C_3H_7O)_2PS(SC_3H_7)$	115-116 (3)	1.4955	1.0561	70.85	18.94	18.72 ± 0.07
9	$(i\text{-}C_3H_7O)_2PS(SC_3H_7\text{-}i)$	91-92 (3)	1.4843	1.0351	70.90	18.99	
10	$(i\text{-}C_4H_9O)_2PS(SC_4H_9\text{-}i)$	148-149 (4)	1.4859	1.0159	84.33	18.57	
11	$(C_2H_5O)_2PS(SCOCH_3)$	98 (2)	1.5154	1.1898	57.89	19.82	
12	$(i\text{-}C_3H_7O)_2PS(SCOCH_3)$	100-101 (3)	1.4979	1.1177	67.21	19.90	
13	$(i\text{-}C_4H_9O)_2PS(SCOCH_3)$	125-126 (3)	1.4929	1.0793	76.56	19.71	
14	$(C_2H_5O)_2PSSCOOCH_3)$	105-106 (3.5)	1.5063	1.2171	59.66	19.95	
15	$(C_2H_5O)_2PS(SCOOC_2H_5)$	115 (4)	1.5001	1.1891	63.90	19.57	19.77 ± 0.03
16	$(C_2H_5O)_2PS(SCOOC_3H_7)$	125 (5.5)	1.4981	1.1620	68.70	19.75	
17	$(C_2H_5O)_2PS(SCOOC_4H_9\text{-}i)$	162-163 (6)	1.4889	1.1281	73.25	19.68	
18	$(C_2H_5O)_2PS(SCOOC_5H_{11}\text{-}i)$	137-138 (4)	1.4925	1.1179	78.04	19.85	
19	$(i\text{-}C_3H_7O)_2PS(SCOOC_2H_5)$	109-109.5 (3)	1.4894	1.1301	73.18	19.61	
20	$(i\text{-}C_3H_7O)_2PS(SCOOC_5H_{11}\text{-}i)$	137-138 (3)	1.4841	1.0773	87.24	19.82	

As mentioned above, the value of the atomic refraction of sulfur bound to phosphorus in the P=S group of trimethyl phosphorothionate is 9.68, i.e., very close to the atomic refraction of thione sulfur, 9.70. If we assume that this value is preserved also in the O,O-dialkyl S-hydrogen phosphorothiolothionates, we may calculate the atomic refractions of thiol sulfur in the groups P–S–H and P–S–R and of thioanhydride sulfur in the group P–S–CO–; the values obtained are 9.12, 9.02, and 10.07 respectively. The second of these values should be compared with the value of 8.12 found by Jones, Davies, and Dyke for trimethyl phosphorothiolate. Whether this lack of agreement ($\Delta = 0.90$) is due to constitutive effects, or to inadequate accuracy in the determination of the refraction of thiol sulfur, which was based by these authors on a single observation, it is, as yet, impossible to say.

We have already [10] described the syntheses of O,O-dialkyl S-hydrogen phosphorothiolothionates and trialkyl phosphorothiolothionates. O,O-Dialkyl S-hydrogen phosphorothiolothionates have been prepared also by Malatesta and Laverone [2]. The S-acyl derivatives of O,O-dialkyl S-hydrogen phosphorothiolothionates were prepared by us in high yields from the corresponding sodium, potassium, or lead salts and acyl halides, for example:

$$[(RO)_2PSS]_2Pb + 2R'COCl \longrightarrow 2(RO)_2PSSCOR' + PbCl_2;$$
$$(RO)_2PSSK + ClCOOR' \longrightarrow (RO)_2PSSCOOR' + KCl.$$

The acetyl derivatives were obtained equally readily from the potassium, sodium, and lead salts. The benzoyl derivative examined could be obtained only from the lead salt; on the other hand, the alkoxycarbonyl derivatives could be obtained only from the alkali-metal salts.

EXPERIMENTAL

O,O-Diethyl S-Acetyl Phosphorothiolothionate was prepared: 1. From Lead Bis[O,O-diethyl phosphorothiolothionate]. Acetyl chloride (7.8 g, i.e. 0.1 mole) was added to 11.5 g (0.02 mole) of lead bis[O,O-diethyl phosphorothiolothionate]. The mixture became warm, and the bulk of the solid present became less. The reaction mixture was heated at 65-80° in a water bath for two hours under reflux. When the mixture was cool, the lead chloride was filtered off and washed with benzene; 5.2 g was obtained (theoretical amount 5.56 g). The filtrate was dried over sodium sulfate and vacuum-fractionated. Two distillations yielded 7.8 g (85%) of a substance of b.p. 98° (2 mm).

O,O-Diethyl S-acetyl phosphorothiolothionate was obtained as an orange liquid; n_D^{20} 1.5154; d_4^{20} 1.1898; found MR 57.89; calculated MR 57.84.

Found %: C 31.55; 31.54; H 5.78; 5.85; P 13.63; 13.60
$C_6H_{13}O_3PS_2$. Calculated %: C 31.58; H 5.70; P 13.60

2. From Potassium O,O-Diethyl Phosphorothiolothionate. Acetyl chloride (11.78 g, i.e. 0.15 mole) was added to 10.12 g (0.05 mole) of potassium O,O-diethyl phosphorothiolothionate. The mixture immediately became warm. The solid present changed from the crystalline (scales) to the amorphous state. The reaction mixture was heated in a water bath at 65-70° for two hours under reflux. When the mixture was cool, the precipitate of potassium chloride was filtered off and washed with benzene; 3.6 g was obtained (theoretical amount 3.7 g). The filtrate was dried over calcined sodium sulfate and vacuum-fractionated. Two fractionations yielded 8.15 g (80%) of a substance boiling at 108-109° (4 mm); n_D^{20} 1.5122; d_4^{20} 1.1894; found MR 57.62; calculated MR 57.84.

O,O-Diisopropyl S-Acetyl Phosphorothiolothionate. This was prepared from 12.6 g (0.02 mole) of lead bis[O,O-diisopropyl phosphorothiolothionate] and 6.3 g (0.08 mole) of acetyl chloride, following the procedure used for O,O-diethyl S-acetyl phosphorothiolothionate; 7.0 g (67%) was obtained. O,O-Diisopropyl S-acetyl phosphorothiolothionate is a light-yellow liquid, b.p. 100-101° (3 mm); n_D^{20} 1.4979; d_4^{20} 1.1177; found MR 67.21; calculated MR 67.08.

Found %: P 12.15; 11.95
$C_8H_{17}O_3PS_2$. Calculated %: P 12.11

O,O-Diisobutyl S-Acetyl Phosphorothiolothionate. This was prepared from 5.28 g (0.02 mole) of sodium O,O-diisobutyl phosphorothiolothionate and 4.71 g (0.06 mole) of acetyl chloride; the yield was 4.0 g (70%). O,O-Diisobutyl S-acetyl phosphorothiolothionate is an orange liquid; n_D^{20} 1.4929; d_4^{20} 1.0793; found MR 76.56; calculated MR 76.62. B.p. 125-126° (3 mm).

Found %: P 10.96; 10.83
$C_{10}H_{21}O_3PS_2$. Calculated %: P 10.91

O,O-Diisopropyl S-Benzoyl Phosphorothiolothionate. Benzoyl chloride (4.2 g, i.e. 0.03 mole) was added to 8.3 g (0.013 mole) of lead bis[O,O-diisopropyl phosphorothiolothionate]. No appreciable change occurred in the reaction mixture at room temperature. When the mixture was heated in a water bath at 70-80°, the precipitate began to diminish in bulk and turned from gray to white; a layer of colorless liquid appeared above the precipitate. The reaction mixture was heated in a water bath until the liquid above the precipitate began to turn yellow (30 minutes). When cool, the whole of the reaction mixture solidified; it was extracted with ether, and the insoluble residue of lead chloride was filtered off; 4.7 g was obtained (theoretical amount 3.6 g). The filtrate was dried over calcined sodium sulfate, and the ether and excess of benzoyl chloride were distilled off under reduced pressure. The residue crystallized out. Recrystallization from ethanol yielded 6.7 g (80%) of O,O-diisopropyl S-benzoyl phosphorothiolothionate, m.p. 51-52°, in the form of fine prisms, slightly pink-lilac in color. It is readily soluble in acetone, ether, carbon tetrachloride, and petroleum ether; insoluble in water.

Found %: P 9.78; 9.54

$C_{13}H_{19}O_3PS_2$. Calculated %: P. 9.75

Preparation of S-Alkoxycarbonyl Derivatives of O,O-Dialkyl S-Hydrogen Phosphorothiolothionates. An excess of alkyl chloroformate was added to potassium or sodium O,O-dialkyl phosphorothiolothionate. Reaction began at room temperature only in the case of methyl chloroformate; the reaction mixture grew warm, the precipitate rapidly became less in bulk, and a layer of colorless liquid appeared. All the other chloroformic esters, from ethyl to isopentyl, reacted only when heated. The reaction mixture was heated for a period varying from 30 minutes to 3-4 hours at a temperature varying from 90° to 140-150°. The precipitate of potassium or sodium chloride was then filtered off and washed with benzene; in all cases the salt was obtained in quantitative yield. The filtrate was dried over sodium sulfate and fractionated under reduced pressure. Yields of 80-90% were obtained of the S-alkoxycarbonyl derivatives.

O,O-Diethyl S-Methoxycarbonyl Phosphorothiolothionate. A mixture of 11.2 g (0.05 mole) of potassium O,O-diethyl phosphorothiolothionate and 9.4 g (0.1 mole) of methyl chloroformate yielded 10.0 g (82%) of O,O-diethyl S-methoxycarbonyl phosphorothiolothionate, b.p. 105-106° (3.5 mm); n_D^{20} 1.5063; d_4^{20} 1.2171; found MR 59.66; calculated MR 59.48.

Found %: P. 12.73; 12.72

$C_6H_{13}O_4PS_2$. Calculated %: P 12.70

O,O-Diethyl S-Ethoxycarbonyl Phosphorothiolothionate. This was obtained in 91% yield (8.7 g) from 8.4 g (0.037 mole) of potassium O,O-diethyl phosphorothiolothionate and 5.4 g (0.05 mole) of ethyl chloroformate. It had b.p. 115° (4 mm); n_D^{20} 1.5001; d_4^{20} 1.1891; found MR 63.90; calculated MR 64.10.

Found %: P 12.04

$C_7H_{15}O_4PS_2$. Calculated %: P 12.01

O,O-Diethyl S-Propoxycarbonyl Phosphorothiolothionate. A mixture of 8.4 g (0.037 mole) of potassium O,O-diethyl phosphorothiolothionate and 6.1 g (0.05 mole) of propyl chloroformate yielded 9.1 g (91%) of O,O-diethyl S-propoxycarbonyl phosphorothiolothionate, b.p. 125° (5.5 mm); n_D^{20} 1.4981; d_4^{20} 1.1620; found MR 68.70; calculated MR 68.72.

Found %: C 36.65; 35.60; H 6.45; 6.40

$C_8H_{17}O_4PS_2$. Calculated %: C 35.27 H 6.25

O,O-Diethyl S-Isobutoxycarbonyl Phosphorothiolothionate. This was prepared from 4.2 g (0.018 mole) of potassium O,O-diethyl phosphorothiolothionate and 5.8 g (0.038 mole) of isobutyl chloroformate. B.p. 162-163° (6 mm); yield 4.3 g (84%); n_D^{20} 1.4889; d_4^{20} 1.1281; found MR 73.25; calculated MR 73.34.

Found %: C 37.98; 37.92; H 6.82, 6.77; P 10.89, 10.87

$C_9H_{19}O_4PS_2$. Calculated %: C 37.76; H 6.64; P 10.84

O,O-Diethyl S-Isopentyloxycarbonyl Phosphorothiolothionate. A mixture of 4.2 g (0.018 mole) of potassium O,O-diethyl phosphorothiolothionate and 7.5 g (0.05 mole) of isopentyl chloroformate yielded 4.3 g (84%) of O,O-diethyl S-isopentyloxycarbonyl phosphorothiolothionate, b.p. 137-138° (4 mm); n_D^{20} 1.4925; d_4^{20} 1.1179; found MR 78.04; calculated MR 77.96.

Found %: C 40.18; 40.20; H 7.12; 7.15; P 10.23; 10.73

$C_{10}H_{21}O_4PS_2$. Calculated %: C 40.00; H 7.00; P 10.34

O,O-Diisopropyl S-Ethoxycarbonyl Phosphorothiolothionate. This was prepared from 8.8 g (0.037 mole) of sodium O,O-diisopropyl phosphorothiolothionate and 5.4 g (0.05 mole) of ethyl chloroformate. B.p. 109-109.5° (3 mm); yield 8.5 g (90%); n_D^{20} 1.4894; d_4^{20} 1.1301; found MR 73.18; calculated MR 73.34.

Found %: C 37.92; 38.00; H 6.75; 6.73; P 10.79; 10.84

$C_9H_{19}O_4PS_2$. Calculated %: C 37.78; H 6.64; P 10.84

O,O-Diisopropyl S-Isopentyloxycarbonyl Phosphorothiolothionate. A mixture of 4.4 g (0.018 mole) of sodium O,O-diisopropyl phosphorothiolothionate and 3.8 g (0.025 mole) of isopentyl chloroformate yielded 5.1 g (90%) of O,O-diisopropyl S-isopentyloxycarbonyl phosphorothiolothionate, b.p. 137-138° (3 mm); n_D^{20} 1.4841; d_4^{20} 1.0773; found MR 87.24; calculated MR 87.19.

Found %: P 9.71; 9.74

$C_{12}H_{25}O_4PS_2$. Calculated %: P 9.45

SUMMARY

1. Values of the group refractions of the two atoms of sulfur in esters and mixed anhydrides of phosphorothiolothionic acid have been determined. The values found for AR_{S_2} are: for O,O-dialkyl S-hydrogen phosphorothiolothionates $(RO)_2PSSH$ 18.82; for trialkyl phosphorothiolothionates $(RO)_2PS(SR)$ 18.72; and for O,O-dialkyl S-acyl phosphorothiolothionates $(RO)_2PSSCOX$ 19.77.

2. The syntheses of S-acyl and S-alkoxycarbonyl derivatives of O,O-dialkyl S-hydrogen phosphorothiolothionates have been described.

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Received June 5, 1953

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* See Consultants Bureau Translation, page 825.
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ACTION OF ALCOHOLS ON BICYCLIC TERPENE OXIDES

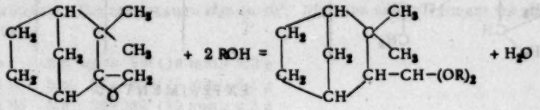
COMMUNICATION 3. ACETALS OF 3-CAMPHENILANECARBOXALDEHYDE

B. A. Arbuzov and L. A. Mukhamedova

In a previous investigation [1] B. A. Arbuzov and Isaeva have shown that, when primary alcohols react with Δ^3-carene oxide in presence of sulfuric acid, they add at the oxide ring with formation of monoethers of the carene glycol (4-alkoxy-3-caranols). When the epoxide is treated with secondary alcohols, reaction proceeds in two directions: in addition to the formation of the normal alcohol addition product, the partial isomerization of the epoxide to an unsaturated aldehyde occurs. With a tertiary alcohol Δ^3-carene oxide reacts with formation only of the unsaturated aldehyde.

The behavior of camphene oxide in this reaction was studied for the case of reaction with methyl alcohol. The main reaction product was the dimethyl acetal of 3-camphenilanecarboxaldehyde. In addition, a small amount of the monomethyl ether of the glycol (3-methoxy-3-camphenilanemethanol) was isolated. No further study was made of the action of alcohols other than methyl alcohol on camphene oxide and its isomerization product (3-camphenilanecarboxaldehyde).

In the present paper we give the results of experiments on the action of alcohols (ethyl, butyl, isobutyl, octyl, and isopropyl) on camphene oxide, and the action of glycols on 3-camphenilanecarboxaldehyde. When the primary alcohols reacted with camphene oxide in presence of sulfuric acid, the corresponding acetals of 3-camphenilanecarboxaldehyde were obtained:



The constants of the acetals obtained are given in Table 1.

TABLE 1

Acetal of 3-camphenilanecarboxaldehyde	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	MR Calc'd	MR Found	Yield %
Diethyl	113-114.5 (8.5)	1.4610	0.9414	65.74	65.95	35.9
Dibutyl	149-151 (6.0)	1.4650	0.9264	84.21	84.26	26.2
Diisobutyl	140-141 (7.0)	1.4612	0.9196	84.21	84.28	36.3
Dioctyl	217-218 (4.0)	1.4665	0.8995	121.15	121.50	28.1

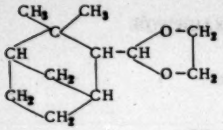
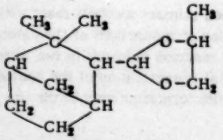
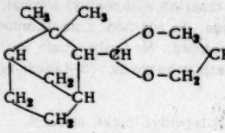
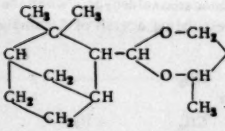
The action of isopropyl alcohol on camphene oxide resulted in the formation of the isomerization product of camphene oxide, 3-camphenilanecarboxaldehyde, as shown by the preparation of its semicarbazone.

In presence of sulfuric acid, therefore, camphene oxide is converted into 3-camphenilanecarboxaldehyde, which gives acetals with primary alcohols. In the case of a secondary alcohol, acetal formation does not occur. Products formed by the addition of alcohols directly to the oxide ring could not be detected

All of the acetals of 3-camphenilanecarboxaldehyde obtained in this way are colorless liquids having a camphorlike odor. With the object of comparing the odor of these acetals with that of cyclic acetals of 3-camphenilanecarboxaldehyde, we prepared some of the latter by the action of glycols on the aldehyde in presence of phosphoric acid. The constants of these acetals are given in Table 2.

All of these cyclic acetals have a camphor odor and are of no interest in perfumery.

TABLE 2

Formula of acetal	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	MR		Yield %
				Cal'd	Found	
	120-121 (14.5)	1.4877	1.0386	54.30	54.44	69.8
	118-119 (12)	1.4805	1.0100	58.92	59.20	86.0
	127.5-128.5 (12)	1.4890	1.0285	58.92	59.03	63.0
	126.5-127.5 (11)	1.4815	1.0013	63.54	63.80	72.0

EXPERIMENTAL

Action of Ethyl Alcohol on Camphene Oxide in presence of Sulfuric Acid. The substances taken for reaction were camphene oxide (15 g), ethyl alcohol (28 g), and sulfuric acid of sp. gr. 1.8 (0.18 g). A solution of the camphene oxide in 9 g of ethyl alcohol was dropped slowly into 19 g of ethyl alcohol containing the sulfuric acid. The temperature of the reaction mixture rose to 40°; when it had fallen again to 18°, the sulfuric acid was neutralized with sodium ethoxide. The alcohol was distilled off, and the residue was vacuum-fractionated from an Arbuzov flask. The following fractions were obtained:

Fraction I b.p. 86-100° (9 mm); 1.3 g
Fraction II b.p. 100-114° (8.5 mm); 5 g; n_D^{20} 1.4650
Fraction III b.p. 114-119° (8.5 mm); 7.4 g; n_D^{20} 1.4622

Two refractionations of Fractions II and III yielded 8 g of a fraction having the following constants: b.p. 113-114.5° (8.5 mm) n_D^{20} 1.4610; d_4^{20} 0.9414; found MR 65.95, calculated at $C_{14}H_{26}O_2$ MR 65.73. It was a colorless, oily liquid, and its constants were not affected by distillation over sodium.

Found %: C 74.15; 74.49; H 11.42; H 11.76
$C_{14}H_{26}O_2$. Calculated %: C 74.28; H 11.58

In order to compare reaction products, 3-camphenilanecarboxaldehyde was treated with ethyl alcohol in presence of sulfuric acid (10 g of the aldehyde and 30 ml of the alcohol). A solution of the 3-camphenilanecarboxaldehyde in 10 ml of ethyl alcohol was dropped slowly into 20 ml of ethyl alcohol containing two drops of sulfuric acid. After neutralization of the sulfuric acid with sodium ethoxide and removal of the alcohol, the residue was vacuum-fractionated. Two fractionations yielded 4 g of a product having the following constants: b.p. 113-115° (8.5 mm); n_D^{20} 1.4612; d_4^{20} 0.9418.

Action of Butyl Alcohol on Camphene Oxide in presence of Sulfuric Acid. The substances taken for reaction were camphene oxide (15 g), butyl alcohol (44 g), and sulfuric acid of sp. gr. 1.8 (0.18 g). A solution of

the camphene oxide in 10 g of butyl alcohol was dropped slowly into 34 g of butyl alcohol containing the sulfuric acid. The temperature of the reaction mixture rose to 48°, and when it had returned to that of the room the sulfuric acid was neutralized with sodium butoxide, the alcohol was distilled off under somewhat reduced pressure (200 mm), and the residue was vacuum-fractionated. Two fractionations resulted in the isolation of 7.3 g of a product having the following constants: B.p. 149-151° (6 mm); n_D^{20} 1.4650; d_4^{20} 0.9264; found MR 84.26; calculated at $C_{15}H_{24}O_2$ MR 84.21. It was a colorless, oily liquid having a camphor odor.

Found %: C 76.32; H 11.91
$C_{15}H_{24}O_2$. Calculated %: C 76.53; H 12.13

Action of Isobutyl Alcohol on Camphene Oxide in presence of Sulfuric Acid. The substances taken for reaction were camphene oxide (15 g), isobutyl alcohol (44 g, i.e. 56 ml), and sulfuric acid of sp. gr. 1.8 (0.17 g). A solution of the camphene oxide in 20 ml of isobutyl alcohol was dropped slowly into 36 ml of isobutyl alcohol containing the sulfuric acid. The temperature of the reaction mixture rose to 50°. After neutralization with sodium isobutoxide and removal of the alcohol, the residue was vacuum-fractionated with the following results:

Fraction I b.p. up to 138° (8 mm); 3 g; n_D^{20} 1.4863
Fraction II b.p. 138 - 140° (8 mm); 5 g; n_D^{20} 1.4682
Fraction III b.p. 140 - 143° (8 mm); 9 g; n_D^{20} 1.4615

Refractionation of Fractions II and III yielded 10.1 g of a fraction having b.p. 140-141° (7 mm); n_D^{20} 1.4612; d_4^{20} 0.9196. Found MR 84.28; calculated at $C_{15}H_{24}O_2$, MR 84.21. The reaction product was a colorless, oily liquid having a camphor odor.

Found %: C 76.18; 76.25; H 12.29; 12.24
$C_{15}H_{24}O_2$. Calculated %: C 76.53; H 12.13

Action of Isopropyl Alcohol on Camphene Oxide in presence of Sulfuric Acid. The substances taken for reaction were camphene oxide (15 g), isopropyl alcohol (42 g), and sulfuric acid of sp. gr. 1.8 (0.17 g). The procedure was as in the previous experiments The temperature rose to 40°. After the usual treatment the residue was vacuum-fractionated, and yielded:

Fraction I b.p. up to 80° (10 mm); 2.3 g
Fraction II b.p. 80 - 83° (10 mm); 8.1 g
Fraction III b.p. 83 - 120° (10 mm); 2.3 g
Residue . . . . . 3.4 g

Fraction II solidified in the condenser.

The Semicarbazone: The substances taken for reaction were the fraction of b.p. 80-83° at 10 mm (1.3 g), semicarbazide hydrochloride (1 g), and sodium acetate (1.5 g). The substance of b.p. 80-83° at 10 mm was added to a solution of the semicarbazide hydrochloride and sodium acetate in a small amount of water, and some methyl alcohol was added to bring the substance into solution. The mixture was shaken vigorously, and a precipitate formed. It was filtered off, washed with water, and dried (2.4 g of crude product). After several recrystallizations from alcohol (methyl and ethyl), the semicarbazone melted at 191-192°. In a mixture melting point test with the semicarbazone of 3-camphenilanecarboxaldehyde there was no depression.

Fraction III was not investigated owing to the small amount available and its extended boiling range.

Action of Octyl Alcohol on Camphene Oxide in presence of Sulfuric Acid. The substances taken for reaction were camphene oxide (10 g), octyl alcohol (43 g), and sulfuric acid (a few drops). The procedure was as in the previous experiments. After neutralization of the reaction mixture with sodium octyloxide and removal of excess of octyl alcohol, the residue was vacuum-distilled, and yielded:

Fraction I b.p. up to 206° (5 mm); 2.9 g; n_D^{20} 1.4740
Fraction II b.p. 207 - 216° (5 mm); 1.5 g; n_D^{20} 1.4712
Fraction III b.p. 216 - 219° (5 mm); 9.1 g; n_D^{20} 1.4672

Refractionation of Fraction III yielded 7.3 g of a substance of b.p. 217-218 (4 mm); n_D^{20} 1.4665; d_4^{20} 0.8995; found MR 121.5; calculated at $C_{18}H_{32}O_2$ MR 121.15. It was a colorless, oily liquid having a camphor odor.

Found %: C 78.96; H 13.07

$C_{20}H_{34}O_2$. Calculated %: C 79.12, H 12.77

Action of Ethylene Glycol on 3-Camphenilanecarboxaldehyde. A drop of orthophosphoric acid was added to a mixture of 10 g of 3-camphenilanecarboxaldehyde and 4.1 g of ethylene glycol. When the mixture was heated at a little above 100°, elimination of water occurred. The water was driven off, the last traces being removed under reduced pressure. Fractionation gave the following results:

Fraction I	b.p. 100 - 110°;	0.8 g
Fraction II	b.p. up to 90° (11.5 mm);	2.5 g
Fraction III	b.p. 90 - 113° (11.5 mm);	0.3 g; n_D^{20} 1.4940
Fraction IV	b.p. 113 - 117° (11.5 mm);	9 g; n_D^{20} 1.4877
	Residue.	0.3 g

Refractionation of Fraction IV yielded a product having the following constants: b.p. 120-121° (14.5 mm); n_D^{20} 1.4877; d_4^{20} 1.0386. Found MR 54.44, calculated at $C_{13}H_{20}O_2$ MR 54.30. It was a colorless, oily liquid having an odor reminiscent of camphor.

Found %: C 73.67; 73.33; H 10.35; 10.29

$C_{13}H_{20}O_2$. Calculated %: C 73.42; H 10.27

Action of 1,2-Propanediol of 3-Camphenilanecarboxaldehyde. A drop of orthophosphoric acid was added to a mixture of 10 g of 3-camphenilanecarboxaldehyde and 5 g of 1,2-propanediol. The procedure was as in the previous experiment. After removal of water, the residue was vacuum-fractionated with the following results:

Fraction I	b.p. 100 - 110°	1.5 g
Fraction II	b.p. up to 80° (13.5 mm);	
Fraction III	b.p. 80 - 119° (13.5 mm);	1.1 g
Fraction IV	b.p. 119 - 121° (13 mm)	11.9 g n_D^{20} 1.4810
	Residue.	0.3 g

Fraction IV was redistilled and yielded a substance having the following constants: b.p. 118-119° (12 mm); n_D^{20} 1.4805; d_4^{20} 1.0100; found MR 59.20; calculated at $C_{13}H_{22}O_2$ MR 58.92. It was a colorless liquid having a camphor odor:

Found %: C 73.81; H 10.69

$C_{13}H_{22}O_2$. Calculated %: C 74.24; H 10.53

Action of 1,3-Propanediol on 3-Camphenilanecarboxaldehyde. A drop of orthophosphoric acid was added to a mixture of 8.6 g of 3-camphenilanecarboxaldehyde and 4.3 g of 1,3-propanediol. After removal of water, the residue was vacuum-fractionated, and yielded:

Fraction I	b.p. 100 - 110°;	1.5 g
Fraction II	b.p. up to 100°; (12 mm);	
Fraction III	b.p. 100 - 125°; (12 mm);	2.5
Fraction IV	b.p. 125 - 129°; (12 mm);	7.5 g; n_D^{20} 1.4890.

Fraction IV was redistilled and yielded a substance having the following constants: b.p 127.5 - 128.5° (12 mm); n_D^{20} 1.4890; d_4^{20} 1.0285; found MR 59.03, calculated at $C_{13}H_{22}O_2$ MR 58.92. It was a colorless liquid having a camphor odor.

Found %: C 73.91; H 10.46

$C_{13}H_{22}O_2$. Calculated %: C 74.24; H 10.53

The Action of 1,3-Butanediol on 3-Camphenilanecarboxaldehyde. The substances taken for reaction were 3-camphenilanecarboxaldehyde (8 g), 1,3-butanediol (4.8 g), and orthophosphoric acid (one drop), and the procedure was as in the previous experiments. The results of the fractionation were as follows:

Fraction I	b.p. 100 - 110°;	(760 mm);	2.4 g
Fraction II	b.p. up to 100°;	(11 mm);	
Fraction III	b.p. 100 - 126°;	(11 mm);	0.3 g
Fraction IV	b.p. 126 - 127.5°;	(11 mm);	8.5 g
	Residue		0.5 g

The constants of Fraction IV were as follows: n_D^{20} 1.4815; d_4^{20} 1.0013; found MR 63.80, calculated at $C_{14}H_{24}O_2$ MR 63.54. It was a colorless liquid having a camphor odor.

Found %: C 74.85; H 10.71

$C_{14}H_{24}O_2$. Calculated %: C 74.95; H 10.78

SUMMARY

1. A study has been made of the reaction of camphene oxide with primary alcohols (ethyl, butyl, isobutyl and octyl) and a secondary alcohol (isopropyl) in presence of sulfuric acid. It has been shown that the reaction of camphene oxide with primary alcohol is accompanied by isomerization of the epoxide and formation, as the sole product, of the corresponding acetals of 3-camphenilanecarboxaldehyde.

2. It has been shown that in the case of secondary alcohols, exemplified by isopropyl alcohol, reaction is again accompanied by isomerization, but it stops at the 3-camphenilanecarboxaldehyde stage, and no acetal formation occurs.

3. By the reaction of 3-camphenilanecarboxaldehyde with glycols (ethylene glycol, 1,2-propanediol, 1,3-propanediol, and 1,3-butanediol) in presence of phosphoric acid, the corresponding cyclic acetals of 3-camphenilanecarboxaldehyde have been prepared

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Received May 18, 1953

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* See Consultants Bureau Translation, page 881.

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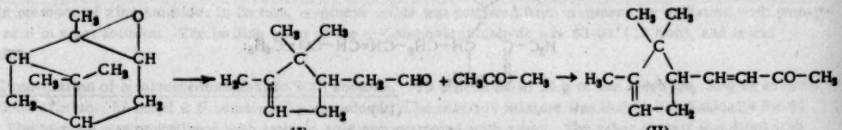
CONDENSATION OF α-CAMPHOLENALDEHYDE WITH KETONES AND ESTERS

B. A. Arbuzov and L. A. Mukhamedova

In presence of zinc bromide, α-pinene oxide readily isomerizes to α-campholenaldehyde (I) [1]. Campholenaldehyde is isomeric with the cyclocitrals, but differs greatly in structure from these substances.

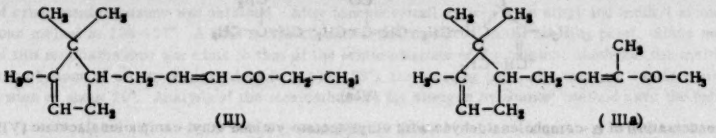


(I) (II)

It would be expected that the condensation of α-campholenaldehyde with acetone would result in the formation of the ketone II, isomeric with the ionones. In order to determine the relation between structure and odor in compounds isomeric with the ionones, we have carried out the condensation of α-campholenaldehyde with acetone and certain other ketones.*

Condensation of α-campholenaldehyde with acetone in presence of aqueous alkali yielded the ketone II, which contained some of the aldol form as impurity. We could not free the material from the latter completely by distillation, but, when the product was distilled over a crystal of camphorsulfonic acid, water was eliminated and, after further distillations, the ketone II was obtained in the pure state. Its constants are as follows: b.p. 132-134° (10 mm); n_D^{20} 1.4893; d_4^{20} 0.9196; found MR 60.40; calculated at $C_{13}H_{20}O$ MR 59.11; ε 1.29. The ketone is an oily liquid having a very slight yellowish-green color and a pleasant odor reminiscent of ionone. The yield of the pure product was 44%. The semicarbazone melted at 136-137°. For the ketone II, B. Sh. Khusnutdinov gave the following constants: b.p. 142° (19 mm); n_D^{20} 1.4835; d_4^{20} 0.9161; MR 59.96; m.p. of semicarbazone 160-161°. These constants, with the exception of the melting point of the semicarbazone, are close to those obtained by us.

The condensation of α-campholenaldehyde with 2-butanone in presence of sodium ethoxide gave poor results. Better results were obtained by the use of aqueous alkali. The reaction product, after removal of the aldol form over camphorsulfonic acid, yielded the ketone $C_{14}H_{22}O$, which had the following constants: b.p. 111.5-113.5° (3 mm); n_D^{20} 1.4910; d_4^{20} 0.9239; found MR 64.68; calculated at $C_{14}H_{22}O$ MR 63.73; ε 0.95. Which of the structures III and IIIa represents this ketone was not ascertained; on the basis of the data in the literature [3], the structure III must be regarded as the more probable.



(III) (IIIa)

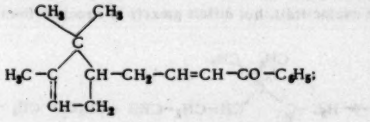
1-(or 3-)Campholenal-2-butanone is a greenish liquid having an odor reminiscent of ionone. Its semicarbazone melted at 203-204°. For this ketone Khusnutdinov gives only b.p. 147° (14 mm); d_4^{20} 0.9421 and m.p. of semicarbazone 203-204°. The boiling point of the ketone and its high specific gravity clearly point to aldol impurity, which we succeeded in removing only by distillation over camphorsulfonic acid.

α-Campholenaldehyde readily reacts with acetophenone in presence of aqueous alkali. The condensation product (IV), after removal of aldol, is a yellowish-green oily liquid having a feeble pleasant odor and the following constants: b.p. 165-166.5° (2 mm); n_D^{20} 1.5495; d_4^{20} 0.9986; found MR 81.04; calculated at $C_{19}H_{22}O$ MR 78.60;

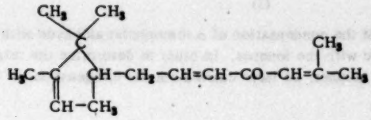
* Some of the syntheses described in this paper were carried out previously in our laboratory by B. Sh. Khusnutdinov, who died in the Great Patriotic War. In his papers there are only a few constants of the compounds, without any description of the conditions of preparation.

ϵ 2.4. For this ketone Khusnutdinov gives the following constants: b.p. 201-202° (12 mm); n_D^{20} 1.5433; d_4^{20} 0.9996, MR 80.2; m.p. of semicarbazone 154-155°.

With mesityl oxide α-campholenaldehyde gave the ketone V, which we did not succeed in obtaining in an analytically pure form. It had the following constants: b.p. 153-155° (6 mm); n_D^{20} 1.5093; d_4^{20} 0.9294; found MR 74.69; calculated for $C_{16}H_{24}O$ Γ_3, MR 72.49; ϵ 2.20. For the ketone V Khusnutdinov gave rather different constants: b.p. 169-171° (10 mm); n_D^{20} 1.5010; d_4^{20} 0.9312; MR 73.46; ϵ 0.96. Such a low value for the exaltation does not agree with the structure of the ketone V, which contains three conjugated bonds. It is clear that Khusnutdinov's product contained aldol impurity.

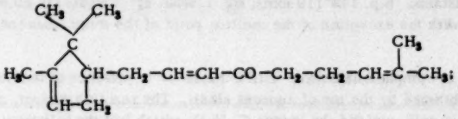


(IV)

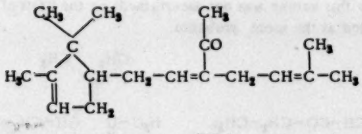


(V)

α-Campholenaldehyde was condensed with 6-methyl-5-hepten-2-one in presence of sodium methoxide. The resulting ketone (VI or VIa), which was isolated in low yield, had the following constants: b.p. 164-166° (5 mm); n_D^{20} 1.4950; d_4^{20} 0.9145; found MR 83.10; calculated for $C_{18}H_{30}O$ Γ_3 MR 81.73; ϵ 1.37. 1-(or 3-)Campholenal-6-methyl-5-hepten-2-one has a feeble pleasant odor. Which of the structures VI and VIa represents this ketone was not ascertained; VI appears to be the more probable.



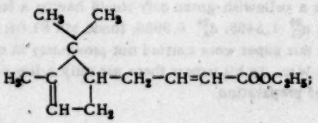
(VI)



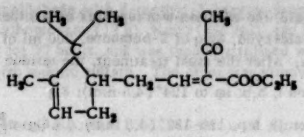
(VIa)

The condensation of α-campholenaldehyde with ethyl acetate yielded ethyl campholenalacetate (VII), which had the following constants: b.p. 126-128° (5 mm); n_D^{20} 1.4745; d_4^{20} 0.9478; found MR 66.00; calculated for $C_{14}H_{22}O_2$ Γ_2 MR 65.37; ϵ 0.63.

The condensation of α-campholenaldehyde with ethyl acetoacetate yielded ethyl 2-campholenalacetoacetate (VIII), which had the following constants: b.p. 132.5-134.5° (2 mm); n_D^{20} 1.4857; d_4^{20} 0.9910; found MR 76.52; calculated for $C_{16}H_{24}O_3$ Γ_2 MR 74.62; ϵ 1.90.



(VII)



(VIII)

EXPERIMENTAL

The α-campholenaldehyde that we used as starting material was obtained by the isomerization of α-pinene oxide in presence of zinc bromide; in its turn, α-pinene oxide was prepared from α-pinene by oxidation with peroxyacetic acid in ether solution. The boiling point of the α-campholenaldehyde was 83-84° (13 mm), and it had n_D^{20} 1.4652.

Condensation of α-campholenaldehyde with acetone. To a mixture of 20 g of the aldehyde, 35 g of acetone, and 300 ml of water, 50 ml of 2 N caustic soda was added. The reaction mixture was shaken mechanically for 60 hours. The mixture was neutralized with tartaric acid and extracted with ether. The ether extract was dried with calcined sodium sulfate, and the ether was drawn off under somewhat reduced pressure. Vacuum fractionation of the residue from an Arbuzov flask yielded the fractions:

Fraction I, b.p. up to 100° (10 mm); 2 g; n_D^{20} 1.4812

Fraction II, b.p. 100-131° (10 mm); 5 g; n_D^{20} 1.4833

Fraction III, b.p. 131-146° (10 mm); 12.8 g; n_D^{20} 1.4882

Residue: 2.1 g of resinous material

Fraction III was refractionated in presence of camphorsulfonic acid, when the formation of water drops in the condenser was noted. The following fractions were obtained:

Fraction I, b.p. up to 131.5° (9 mm); 1.2 g; n_D^{20} 1.4870

Fraction II, b.p. 131-133.5° (9 mm); 11 g; n_D^{20} 1.4892

A further fractionation yielded a product having the following constants: b.p. 132-134° (10 mm); n_D^{20} 1.4893; d_4^{20} 0.9196; found MR 60.40; calculated for $C_{13}H_{20}O$ F_2 MR 59.11; ε 1.29. It was an oily liquid having a feeble yellowish-green color and a pleasant odor, reminiscent of ionone.

Found %: C 80.78; H 10.47

$C_{13}H_{20}O$. Calculated %: C 81.17; H 10.48

Preparation of the semicarbazone. The substances taken for reaction were semicarbazide hydrochloride (1 g), sodium acetate (1.5 g), and the condensation product from acetone and α-campholenaldehyde (1.7 g); and 2.1 g of crude semicarbazone was obtained. After four recrystallizations from ethyl and methyl alcohols, the semicarbazone melted at 136-137°. A fifth recrystallization had no effect on the melting point. Since the melting point of this semicarbazone was close to that of the semicarbazone of the original aldehyde (the melting point of the semicarbazone of α-campholenaldehyde is 137-138°), the melting point of a mixture was determined; it showed a depression of about 20°. Analysis of the semicarbazone for nitrogen by Dumas' method gave the following results:

Found %: N 17.19

$C_{14}H_{23}ON_3$. Calculated %: N 16.86

Condensation of α-campholenaldehyde with 2-butanone. A solution of 2 g of sodium in 40 ml of ethyl alcohol was added to a mixture of 17 g of the aldehyde and 8 g of 2-butanone. The solution rapidly turned dark red, and its temperature rose to 50°. Two minutes after the addition of the ethoxide solution, the mixture was neutralized with tartaric acid. After dilution with water, the reaction mixture was extracted with ether, and the ether layer was dried with sodium sulfate. After removal of ether by suction, the residue was vacuum-fractionated, and yielded:

Fraction I, b.p. up to 141° (10 mm); 4 g

Fraction II, b.p. 141-143° (10 mm); 2.5 g; n_D^{20} 1.4860

Fraction III, b.p. 143-155° (10 mm); 1.7 g; n_D^{20} 1.4868

Residue: 12.5 g

In view of the unsatisfactory yield, the reaction was repeated by another method. The reaction mixture, which was prepared from 17 g of the aldehyde, 30 g of 2-butanone, 300 ml of water and 45 ml of 2 N caustic soda, was shaken mechanically for 60 hours. After the usual treatment, the residue was vacuum-fractionated, and yielded:

Fraction I, b.p. up to 124° (4.5 mm); 8 g

Fraction II, b.p. 125-132° (4.5 mm); 13.6 g; n_D^{20} 1.4885

Residue: 1.2 g

Fraction II was distilled with camphorsulfonic acid, and an appreciable number of water drops were observed in the condenser tube. A further fractionation yielded 10.3 g of a product having the following constants: b.p. 111.5-113.5° (3 mm); n_D^{20} 1.4910; d_4^{20} 0.9239; found MR 64.68; calculated for $C_{14}H_{22}O$ F_2 MR 63.73; ϵ 0.95. It was a slightly greenish, oily liquid having an odor of cedarwood. After dilution, it had an odor reminiscent of ionone.

Found %: C 81.43; H 10.92

$C_{14}H_{22}O$. Calculated %: C 81.52; H 10.75

Preparation of the semicarbazone. The substances taken for reaction were semicarbazide hydrochloride (1 g), sodium acetate (1.5 g), and the condensation product from α-campholenaldehyde and 2-butanone (1.8 g); and after 30 minutes the semicarbazone was precipitated. It was filtered off, washed with water, and dried (2.8 g of crude product). After three recrystallizations, the semicarbazone melted at 203-204°. A fourth recrystallization had no effect on the melting point. Analysis of the semicarbazone for nitrogen by Dumas' method gave the following results:

Found %: N 16.26

$C_{15}H_{25}ON_3$. Calculated %: N 15.95

Condensation of α-campholenaldehyde with acetophenone. To a mixture of 18.7 g of the aldehyde, 25 g of acetophenone, and 300 ml of water, 50 ml of 2 N caustic soda was added. The reaction mixture was shaken mechanically for 75 hours. After neutralization with tartaric acid, the solution was extracted with ether, and the ether layer was dried with sodium sulfate. After removal of ether under suction, the residue was vacuum-fractionated, and yielded:

Fraction I, b.p. up to 100° (13 mm); 20 g

Fraction II, b.p. 100-170° (13-6 mm); 3.7 g; n_D^{20} 1.5130

Fraction III, b.p. 170-190° (6 mm); 12.4 g; n_D^{20} 1.5430

Residue: 1.5 g

Fraction I consisted of unchanged starting materials. Fractions II and III were redistilled with camphorsulfonic acid. As a result of a third distillation 9.6 g of a product was obtained having the following constants: b.p. 165-166.5° (2 mm); n_D^{20} 1.5495; d_4^{20} 0.9986; found MR 81.04; calculated for $C_{18}H_{22}O$ F_5 MR 78.60; ϵ 2.4. It was an oily liquid, yellowish-green in color, and having a feeble spicelike odor.

Found %: C 84.60; H 9.07

$C_{18}H_{22}O$. Calculated %: C 85.04; H 8.72

Condensation of α-campholenaldehyde with mesityl oxide. Sodium methoxide (0.2 g of sodium in 2 ml of methyl alcohol) was added to a mixture of 17.5 g of the aldehyde and 14 g of mesityl oxide. The temperature in the reaction flask rose to 62°. After three minutes the solution was neutralized with tartaric acid, diluted with water, and extracted with ether. The ether layer was dried with sodium sulfate. After removal of ether under suction, the residue was vacuum-fractionated, and yielded:

Fraction I, b.p. up to 100° (7 mm); 4.9 g

Fraction II, b.p. 100-161° (8 mm); 4.0 g; n_D^{20} 1.4855

Fraction III, b.p. 161-169° (8 mm); 6.5 g; n_D^{20} 1.4995

Fractions II and III were distilled with camphorsulfonic acid. A further fractionation of these fractions gave 5.1 g of a substance having the following constants: b.p. 153-155° (6 mm); n_D^{20} 1.5093; d_4^{20} 0.9294; found MR 74.69; calculated for $C_{16}H_{24}O$ F_3 MR 72.49; ϵ 2.20. It was a yellow, oily liquid having a feeble, spicelike odor.

Found %: C 82.12; 82.22; H 10.61, 10.68

$C_{16}H_{24}O$. Calculated %: C 82.70; H 10.41

Condensation of α-campholenaldehyde with 6-methyl-5-hepten-2-one. The substances taken for reaction were the aldehyde (19 g), the methylheptenone (17 g), water (300 ml), and 2 N caustic soda (50 ml). The reaction mixture was agitated mechanically for 77 hours, and was then neutralized with tartaric acid and extracted with ether. The ether layer was dried with sodium sulfate. The ether was removed under suction, and the residue was vacuum-fractionated, yielding:

Fraction I, b.p. 61-110° (10-5 mm); 21.4 g

Fraction II, b.p. 110-158° (4 mm); 2.2 g

Fraction III, b.p. 158-170° (4-7 mm); 9.2 g; n_D^{20} 1.4840

There was a small amount of resinous residue. Fraction III was fractionated three times more (once with camphorsulfonic acid), but on every occasion partial decomposition occurred, even when an initial residual pressure of 2 mm was attained. As a result, the distillate was contaminated with decomposition products. The resulting product boiled at 146-151° (4-4.5 mm).

In order to obtain the substance in the pure state, the reaction was repeated. To the 21.4 g of Fraction I, b.p. 61-110° (10 mm), which consisted mainly of a mixture of the starting materials, a solution of 0.2 g of sodium in methyl alcohol (2 mm) was added. The temperature rose from 18° to 52°. After three minutes the solution was neutralized with tartaric acid. The mixture was extracted with ether, and the ether layer was dried. After removal of ether under suction, the residue was vacuum-fractionated from an Arbuzov flask in presence of a crystal of camphorsulfonic acid. The following fractions were obtained:

Fraction I, b.p. up to 160° (4-5 mm); 7 g

Fraction II, b.p. 160-180° (5-9 mm); 6.2 g; n_D^{20} 1.4800

Fraction III, b.p. 180-184° (9-10 mm); 3.4 g; n_D^{20} 1.4950

A small amount of resinous material remained as residue. It was not found possible to obtain a pure product from Fraction II, since decomposition occurred during distillation. The constants of Fraction III were as follows: n_D^{20} 1.4950; d_4^{20} 0.9160, found MR 83.40; calculated for $C_{18}H_{28}O$ F_3 MR 81.73; ε 1.37. Fraction III was redistilled, and yielded:

Fraction I, b.p. 164° (5 mm)

Fraction II, b.p. 164-166° (5 mm); 2.1 g

The constants of the substance of b.p. 164-166° (5 mm) were as follows: n_D^{20} 1.4950; d_4^{20} 0.9145; found MR 83.10; calculated for $C_{18}H_{28}O$ F_3 MR 81.73; ε 1.37. It was a colorless, or very slightly yellowish, liquid having a faint pleasant odor.

Found %: C 83.16; H 11.24

$C_{18}H_{28}O$. Calculated %: C 83.01; H 10.84

Condensation of α-campholenaldehyde with ethyl acetate. Sodium dust (6 g) was prepared under toluene. The toluene was poured off, and 128 ml of ethyl acetate, previously cooled to a temperature of −10 to −15°, was poured over the sodium. The contents of the flask were cooled to −10 to −15°, and the aldehyde (20 g) was dropped in over a period of one hour. The temperature of the cooled mixture was not allowed to rise above −10°. When the whole of the sodium had dissolved, 18 ml of glacial acetic acid was added, and the mixture was carefully diluted with water. The ethyl acetate layer was separated, and the aqueous layer was extracted with ether. The united extracts were washed with dilute hydrochloric acid, with water, with a very dilute solution of sodium bicarbonate, and again several times with water. The solution was dried with sodium sulfate, solvent was distilled off, and the residue was vacuum-fractionated, yielding:

Fraction I, b.p. up to 115° (10 mm); 3.1 g

Fraction II, b.p. 115-135° (9.5 mm); 1.2 g; n_D^{20} 1.4685

Fraction III, b.p. 136-139° (9.5 mm); 8.5 g; n_D^{20} 1.4740

Residue: 8.9 g of resin

Fraction III was redistilled, and yielded 6.8 g of an ester having the following constants: b.p. 126-128° (5 mm); n_D^{20} 1.4745; d_4^{20} 0.9478; found MR 66.00; calculated for $C_{14}H_{22}O_2$ F_2 MR 65.37; ε 0.63.

Found %: C 75.46; H 9.99

$C_{14}H_{22}O_2$. Calculated %: C 75.62; H 9.98

Condensation of α-campholenaldehyde with ethyl acetoacetate. A mixture of 22 g of α-campholenaldehyde and 19 g of ethyl acetoacetate was cooled to −15°, and 1.5 g of piperidine was added. The mixture was allowed to stand in the cold. After 48 hours, the mixture was neutralized with dilute sulfuric acid, washed with water, and extracted with ether. The ether layer was dried with sodium sulfate. After removal of ether under suction, the residue was vacuum-fractionated, and yielded:

Fraction I, b.p. up to 115° (5 mm)

Fraction II, b.p. 115-157° (5 mm); 1 g; n_D^{20} 1.4770

Fraction III, b.p. 157-162° (6 mm); 17.2 g; n_D^{20} 1.4825

Residue: 7 g of resin

After three fractionations, Fraction III yielded the condensation product (12.9 g), which had the following constants: b.p. 132.5-134.5° (2 mm); n_D^{20} 1.4857; d_4^{20} 0.9910; found MR 76.52; calculated for $C_{13}H_{24}O_3$ MR 74.62; ε 1.90. It was a faintly yellowish, oily liquid of pleasant odor.

Found %: C 72.38; 72.43; H 9.29; 9.49

$C_{13}H_{24}O_3$. Calculated %: C 72.69; H 9.15

SUMMARY

1. By the condensation of α-campholenaldehyde in alkaline medium with acetone, 2-butanone, acetophenone, mesityl oxide, and 6-methyl-5-hepten-2-one, the corresponding unsaturated ketones have been prepared. In spite of the considerable difference from the isomeric ionones in structure, campholenalacetone has an odor close to that of the ionones. The other ketones have pleasant spicelike odors.

2. α-Campholenaldehyde condenses with ethiy acetate and with ethyl acetoacetate yielding ethyl campholenalacetate and ethyl 2-campholenalacetoacetate, respectively.

Received May 18, 1953

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DETERMINATION OF THE INDIVIDUAL HYDROCARBON COMPOSITION OF GASOLINES BY THE COMBINATION METHOD

COMMUNICATION 4. GASOLINE FROM TUIMAZIN PETROLEUM*

B. A. Kazansky, G. S. Landsberg, A. F. Plate, P. A. Bazhulin, E. A. Mikhailova, A. L. Liberman, M. M. Sushchinsky, G. A. Tarasova, S. A. Ukholin, and S. V. Voronko

In this paper we present the results of a study of the individual composition of a gasoline having a boiling limit of 150° from low-sulfur Tuimazin petroleum (Devonian level). The investigation was carried out by the previously described combination method [1], which has been used in the study of two gasolines from Kazanbulak [2] and two Surakhan gasolines [3]. Unlike the Surakhan gasolines, the gasoline studied in the present investigation was obtained directly from the petroleum by distillation in the laboratory, as also were the Kazanbulak gasolines. On account of the increase in the number of hydrocarbons that have now been synthesized and studied spectrographically, and also on account of the perfection of the technique in its separate stages, we have succeeded in accounting for the hydrocarbon composition of the gasoline more completely and in reducing the time required in the actual investigation. Also, in this and subsequent investigations, with the object of improving the optical method and making it more rapid, we have introduced a photoelectric method [4] for measuring the intensities of the Raman lines. Parallel determinations by the photographic and photoelectric methods of measurement for a number of fractions gave satisfactorily agreeing results.

TABLE 1

Distribution by Classes by the Hydrocarbons Found

Class of hydrocarbon	No. of hydrocarbons in the gasoline
Paraffins	20
Cyclopentanes	5
Cyclohexanes	13
Aromatics	6
	44

As a result of this investigation, the gasoline from Tuimazin petroleum has been accounted for to the extent of 87.9% (by weight on the whole gasoline). Altogether, forty-four hydrocarbons have been found in this gasoline, and their contents have been determined quantitatively. Their distribution by classes is given in Table 1.

In what follows, the gasoline from Tuimazin petroleum will be denoted by TsT-2. The letters used to denote the fractions are the same as those used in the papers referred to above [1, 2, 3]. The contents of all of the individual hydrocarbons found in the gasoline have been calculated as percent by weight of the "whole gasoline", and the values are given in Table 2. In the same table the general quantitative balance sheet of the whole investigation is given. The results in Table 2 permit the group composition of the gasoline to be determined, taking into separate account the normal and branched paraffins, and also the cyclopentane and cyclohexane hydrocarbons. This is shown in Table 3.

As can be seen from Table 2 and 3, the gasoline TsT-2 contains 66.2% of paraffins and 16.5% of naphthene hydrocarbons. Of the paraffin-naphthene part of the gasoline TsT-2, 80% consists of paraffins. Hence, the gasoline from Tuimazin petroleum is a paraffin-base gasoline in composition; also, 59.5% of the paraffin component consists of normal paraffins.

The ratio of the amounts of cyclopentane and cyclohexane hydrocarbons in the naphthene part is 0.48.

The branched-paraffin component is made up of 97.5% of paraffins having a tertiary carbon, and only 2.5% of paraffins having a quaternary carbon. Hence, hydrocarbons having a tertiary carbon predominate among the branched paraffins. Also, among paraffins having tertiary carbon atoms, there is a complete absence in the gasoline TsT-2 of hydrocarbons having two or three tertiary carbon atoms.

When the paraffin composition is examined by groups of hydrocarbons of equal molecular weight, it will be seen that, of the C_8 and C_8 hydrocarbons, the gasoline contains all possible isomers except 2,3-dimethylbutane. Of the C_7 hydrocarbons, all the dimethylpentanes and 3-ethylpentanes are absent in the gasoline TsT-2. Of the C_8

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TABLE 2

Individual Hydrocarbons Found in the Gasoline TsT-2

Hydrocarbon	Content (% by weight)	Hydrocarbon	Content (% by weight)
Paraffin Hydrocarbons			
Propane	0.98	Heptane	9.74
Butane	4.69	2-Methylhexane	2.47
Isobutane	0.70	3-Methylhexane	3.43
Pentane	6.32	Octane	7.12
2-Methylbutane	3.57	2-Methylheptane	4.69
Neopentane (?)	0.49	3-Methylheptane	1.71
Hexane	8.43	4-Methylheptane	0.80
2-Methylpentane	3.06	Nonane	2.05
3-Methylpentane	2.40	3-Methyloctane	1.18
2,2-Dimethylbutane	0.17	4-Methyloctane	2.15
		Total	66.2
Cyclopentane Hydrocarbons			
Cyclopentane	0.37	cis-1,2-Dimethylcyclopentane	0.48
Methylcyclopentane	2.44	trans-1,2-Dimethylcyclopentane	1.36
Ethylcyclopentane	0.72		
		Total	5.4
Cyclohexane Hydrocarbons			
Cyclohexane	1.21	1-Ethyl-2-methylcyclohexane	0.09
Methylcyclohexane	3.74	1-Ethyl-3-methylcyclohexane	0.25
Ethylcyclohexane	0.70	1-Ethyl-4-methylcyclohexane	0.12
1,1-Dimethylcyclohexane	0.13	1,1,3-Trimethylcyclohexane	2.68
1,2-Dimethylcyclohexane	0.49	1,2,4-Trimethylcyclohexane	0.09
1,3-Dimethylcyclohexane	1.10	1,3,5-Trimethylcyclohexane	0.03
1,4-Dimethylcyclohexane	0.43		
		Total	11.1
Aromatic Hydrocarbons		Accounted for (% on TsT-2)	87.9
Benzene	0.53	Not accounted for	2.3
Toluene	1.85	Sulfur compounds and losses	1.6
Ethylbenzene	0.53	Residues in flasks after fractionation	2.5
o-Xylene	0.59	Losses	5.7
m-Xylene	1.26		
p-Xylene	0.42		
Total	5.2	Total (% on TsT-2)	100.0

TABLE 3

Group Composition of the Gasoline TsT-2

Class of hydrocarbons	Content (% on TsT-2)
Normal paraffins	39.3
Paraffins having a tertiary carbon	26.2
Paraffins having a quaternary carbon	0.7
Cyclopentanes	5.4
Cyclohexanes	11.1
Aromatics	5.2

hydrocarbons, octane and all three methylheptanes are present. The more branched octane isomers are absent from the gasoline. Of the C_9 paraffins, only three were found: nonane and 3- and 4-methyloctanes.

The content of cyclopentane hydrocarbons in the gasoline TsT-2 is low, and has the value 5.4%. The content of cyclopentane itself is extremely low (0.37%). Among the cyclopentane hydrocarbons having one side chain there is a predominance of methylcyclopentane, and among those having two side chains, only cis- and trans-1,2-dimethylcyclopentanes are found in the gasoline TsT-2, the trans-form predominating. It should be noted that there is an increase of the percent content of cyclopentane hydrocarbons with increase in their molecular weights.

The content of cyclohexane hydrocarbons in the gasoline TsT-2 is 11.1%. The comparatively high content of methylcyclohexane (3.74%) with respect to the other members of this class is noteworthy.

Of the cyclohexanes containing two methyl groups, 1,3-dimethylcyclohexane is present in the greatest amount, and 1,2- and 1,4-dimethylcyclohexanes are present in equal amounts. Among the ethylmethylcyclohexanes, again there is an appreciable predominance of the hydrocarbon with side chains in 1,3-orientation. Among trimethylcyclohexanes, 1,1,3-trimethylcyclohexane, which has a quaternary carbon atom, predominates in the gasoline.

The content of aromatic hydrocarbons in the gasoline TsT-2 is 5.2%, and is close to the content of cyclopentane hydrocarbons (5.4%). In order of reducing contents, the individual aromatic hydrocarbons fall into the following series: toluene, m-xylene, o-xylene, ethylbenzene, benzene, and p-xylene. As in the case of the cyclohexane hydrocarbons, there is a predominance of aromatic hydrocarbons having one side chain, or two in meta orientation. Also, as in the case of the cyclopentane hydrocarbons, the percent content of the aromatic hydrocarbons rapidly increases with increase in molecular weight.

EXPERIMENTAL

Preparation of the wide fraction ShT-2, and its fractionation. The petroleum was distilled from copper vessels, and yielded Fraction Sh, with a boiling limit of 200°. The gaseous hydrocarbons that came off were collected in traps cooled to −70°, and at the end of the fractionation they were united to the distillate. Fraction ShT-2 (boiling limit 200°) so obtained, had the following properties: n_D^{20} 1.4087; d_4^{20} 0.7279; aniline point 59.1°; sulfur content 0.059% by weight.*

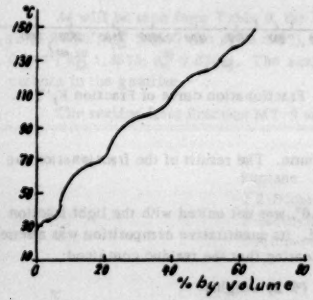

Fig. 1. Fraction curve for the gasoline ShT-2

The results obtained in the fractionation of the wide fraction through a 25-plate column are given in Table 4 and Fig. 1.

The fraction At-2 had the following properties: n_D^{20} 1.4036; d_4^{20} 0.7186; aniline point 57.6°; sulfur content 0.0095% by weight. From this point on, all calculations on the contents of individual hydrocarbons and fractions obtained at various stages of the investigation were based on the "whole" gasoline, TsT-2, which consisted of Fractions K_1, L, and A, i.e., all that comes over below 150°. In this investigation, the amount of TsT-2 was 1088.6 g.

Investigation of the gases and the light fraction. The gaseous part K_1T-2 and the light fraction LT-2 contained sulfur compounds. In order to remove the readily volatile sulfur compounds, the tube containing the gaseous part K_1T-2 was connected to a system consisting of a train of wash-vessels containing concentrated solutions

TABLE 4

Fractionation of the Gasoline ShT-2

Fraction	Boiling limits (°C at 760 mm)	Weight (g)	Content of fraction (% by weight) in ShT-2	Content of fraction (% by weight) in TsT-2
Amount taken for fractionation. . .	–	1518	100.00	
Gaseous part K_1T-2	–	99.6	6.56	9.15
Light fraction LT-2	19.6-44.0	100	6.59	9.19
Main fraction AT-2	44.0- 150	889	58.56	81.66
Residue	Above 150	403	26.55	
Losses	–	26.4	1.74	

* The sulfur content was determined by the lamp combustion method.

of caustic soda and sulfuric acid, a silica-gel tower, and some traps in the form of coils cooled by liquid air. The gases were slowly passed through this system and condensed in the traps. In order to expel the gaseous hydrocarbons, nitrogen was passed through the system. The tube and traps were weighed before and after the experiment. A tube containing Fraction LT-2 was then attached to the system, and toward the end of the experiment the tube was heated to 30°. The gas evolved was collected in the same traps together with the gas from the gaseous fraction K_1T-2, and this gas also was expelled from the system with nitrogen. The united purified gases were denoted by K_1', and the united unevaporated residues were denoted by L'. The results of the experiments on the purification of the gases of Fractions K_1T-2 and LT-2 from sulfur compounds are given in Table 5.

TABLE 5

Purification of the Gases of K_1T-2 from Sulfur Compounds

Fraction	Weight (g)			Content of fraction (% by weight)	
	K_1T-2	LT-2	total	in K_1 + L	in TsT-2
Amount taken for purification	49.8	50.0	99.8	100.0	18.33
Gas K_1'	37.3	0	37.3	37.37	6.85
Light fraction L'T-2	11.0	49.96	60.96	61.08	11.20
Sulfur compounds and losses	1.5	0.04	1.54	1.54	0.28

TABLE 6

Fractionation of the Gas K_1'T-2

Hydrocarbon	Weight (g)	Content of hydrocarbons (% by weight)	
		in K_1'T-2	in TsT-2
Amt. taken for fractionation	8.0	100.0	6.85
Propane	1.146	14.32	0.98
Isobutane	0.813	10.16	0.70
Butane	4.944	61.80	4.24
Neopentane (?)	0.144	1.80	0.12
Residue of b.p. above 16°	0.77	9.62	0.66
Losses	0.18	2.30	0.15

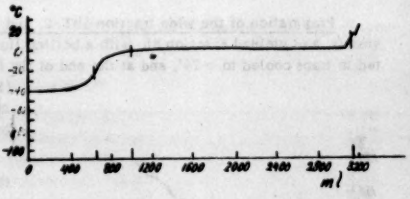

Fig. 2. Fractionation curve of Fraction K_1'T-2.

The purified gas K_1'T-2 was fractionated through a Podbielniak column. The results of the fractionation are given in Table 6 and in Fig. 2.

The residue from the fractionation of the gas, which boiled above 16°, was not united with the light fraction L'T-2 (as required by the scheme [1]) owing to the small amount obtained. Its quantitative composition was assessed on the basis of its refractive index, which was found to be n_D^{20} 1.3541, indicating that the residue contained:

	(% by weight)	
	in residue	in TsT-2
Isopentane	88.85	0.59
Pentane	11.15	0.07

The light fraction L'T-2 also contained sulfur compounds, and these were removed by an adsorption method. The fraction was passed at −10 to −45° through an adsorption column filled with silica gel, and was eluted with alcohol. The results of these experiments are given in Table 7.

The removal of gas (debutanization) from the desulfurized light fraction was also carried out through a Podbielniak column. The results of the fractionation are given in Table 8.

Investigation of the debutanized Fraction MT-2. Fraction MT-2 was fractionated through a 40-plate column, the fractionation curve (Fig. 3) being determined at the same time. The amounts of the fractions and their properties are given in Table 9.

TABLE 7

Adsorption Separation of Sulfur Compounds from the Light Fraction L'T-2

Fraction	Weight (g)	Content of fraction (% by weight)	
		in fraction L'T-2	in TsT-2
Amt. of L'T-2 passed	60.96	100.0	11.20
Desulfurized light fraction L_1'T-2	58.28	95.60	10.71
Sulfur compounds and losses	2.68	4.40	0.49

TABLE 8

Debutanization and Fractionation of the Desulfurized Light Fraction L_1'T-2

Hydrocarbon	Weight (g)	Content of hydrocarbon (% by weight)	
		in L_1'T-2	in TsT-2
Amt. taken for fractionation	58.3	100.0	10.71
Butane	1.60	2.74	0.29
Neopentane (?)	2.01	3.45	0.37
Debutanized light fraction MT-2	54.13	92.85	9.94
Losses	0.59	0.96	0.11

TABLE 9

Fractionation of the Light Fraction MT-2

Fraction No.	Boiling limits in °C (760 mm)	Weight (g)	n_D^{20}	d_4^{20}	Aniline point (°C)	Content of fraction (by weight)	
						in MT-2	in TsT-2
	Amt. taken for fractionation	51.10	–	–	–	100.0	9.94
	Butane (in trap)	0.80	–	–	–	1.57	0.16
I	25.0-32.0	15.30	1.3537	0.6187	76.9	29.94	2.98
II	32.0-36.05	24.35	1.3580	0.6255	70.8	47.65	4.74
Residue		5.4	1.3673	0.6454	65.0	10.57	1.05
Losses		5.25				10.27	1.02

As will be seen from Table 9, the constants of Fraction I correspond exactly to those of pure 2-methylbutane (b.p. 27.85°; n_D^{20} 1.3537 and d_4^{20} 0.6197), and the constants of Fraction II are close to those of pure pentane (b.p. 36.07°; n_D^{20} 1.3575; d_4^{20} 0.6262). The amounts of these fractions, therefore, correspond to the contents of these hydrocarbons in the gasoline.

The residue from Fraction MT-2 was shown by Raman spectra investigation to contain:

	In residue (%)	In TsT-2 (%)
Pentane	65	0.68
2,2-Dimethylbutane	10	0.10
2-Methylpentane	10	0.10
Cyclopentane	15	0.16

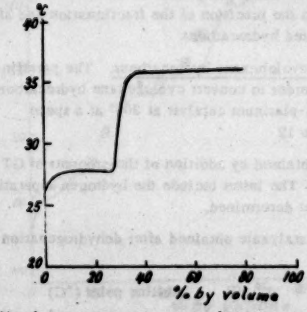

Fig. 3. Fractionation curve of Fraction MT-2

Separation of the aromatic hydrocarbons from the mixture of paraffins and naphthenes in the main fraction AT-2. Fraction AT-2 was subjected to chromatographic adsorption separation with the aid of silica gel into aromatics (BT-2) and the paraffin-naphthene part (VT-2). Since the content of aromatics in Fraction AT-2 was low (10% by volume), an intermediate fraction was taken in the adsorption separation. In order to effect complete separation, the intermediate fraction was again subjected to chromatographic adsorption, pentane being used as displacing liquid. The results of the separation are given in Table 10.

In Table 10 both the actual and the corrected amounts of the fractions are given; the latter are obtained from the former by addition of the actual amounts of the fractions that were used for the qualitative tests for aromatic hydrocarbons and for refractive index determinations.

TABLE 10

Chromatographic Resolution of Fraction AT-2

Amt. of Fraction AT-2(g)	Separation results										
	Aromatics BT-2				Paraffin-naphthene part VT-2				Losses		
	actual (g)	corr. (g)	% in AT-2	% in TsT-2	actual (g)	corr. (g)	% in AT-2	% in TsT-2	(g)	% in AT-2	% in TsT-2
785.2	49.1	51.9	6.6	5.39	723.7	725.07	92.3	75.41	8.3	1.1	0.86

The fractions isolated had the following properties:

	n_D^{20}	d_4^{20}	Aniline point (°C)	Sulfur content (% by weight)
BT-2	1.4946	0.8617	–	~0.02
VT-2	1.3983	0.7096	63.7	0

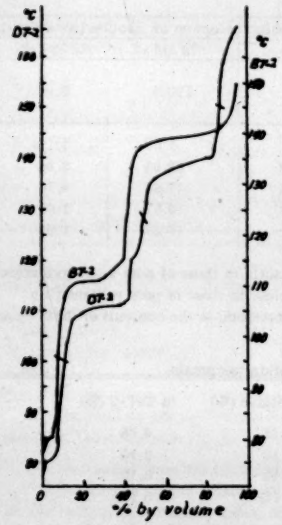

Fig. 4. Fractionation curves of the aromatic fractions BT-2 and DT-2.

The dearomatized fraction did not contain sulfur. The aromatic fraction BT-2 contained about 0.02% of sulfur, i.e., about 7% of the whole of the sulfur contained in the original gasoline AT-2.

Investigation of the aromatics BT-2. The aromatic hydrocarbons BT-2 were fractionated through a column having an efficiency of about 40 theoretical plates. The fractions corresponding to benzene, toluene, and the xylenes were separated, and the fractionation curve was determined at the same time (Fig. 4). The xylene fraction was investigated with the aid of Raman spectra. The results of the fractionation, the properties of the fractions, and the results of the optical analysis are given in Table 11. In order to drive the whole of the xylene fraction from the flask, towards the end of the distillation some pure decahydronaphthalene was added.

Results of the optical analysis of Fraction III

	Content of hydrocarbons (% by wt.) in Fraction III	in TsT-2
o-Xylene	21	0.59
m-Xylene	45	1.26
p-Xylene	15	0.42
Ethylbenzene	19	0.53

It can be seen from these results that, in accordance with its physical properties, Fraction I can be regarded as the benzene fraction, and Fraction II as the toluene fraction. It may, therefore, be assumed that the amounts of these fractions correspond to the contents of benzene and toluene in the gasoline. The presence of sulfur compounds in the fractions of the aromatics BT-2 interfered with the precision of the fractionation and affected the constants of the separated hydrocarbons.

Dehydrogenation of the cyclohexane hydrocarbons. The paraffin-naphthene fraction VT-2 was subjected to catalytic dehydrogenation in order to convert cyclohexane hydrocarbons into aromatics. The fraction VT-2 was passed continuously over an iron-platinum catalyst at 300° at a space velocity of 0.8-1.0 for 24 hours. The results obtained are given in Table 12

In Table 12 the corrected amounts of the catalyzate GT-2 were obtained by addition of the amounts of GT-2 used for refractive index determinations to the actual amounts of GT-2. The losses include the hydrogen separating during dehydrogenation of cyclohexane hydrocarbons; the amount was not determined.

The physical properties of the original Fraction VT-2 and of the catalyzate obtained after dehydrogenation (GT-2) were as follows:

	n_D^{20}	d_4^{20}	Aniline point (°C)
VT-2	1.3983	0.7096	63.7
GT-2	1.4040	0.7165	57.1

TABLE 11

Fractionation of the Aromatics BT-2

Fraction No.	Boiling limits in °C (760 mm)	Weight (g)	n_D^{20}	d_4^{20}	Content of fraction (by weight) in BT-2	Content of fraction (by weight) in TsT-2
Amount taken for fractionation.		48.5	1.4946	0.8617	100.0	5.39
I	76.7- 99.9	4.8	1.4922	0.8607	9.90	0.53
II	99.9-127.9	16.65	1.4933	0.8609	34.33	1.85
III	127.9-150.4	25.25	1.4965	0.8646	52.06	2.81
Residue.		1.3			2.68	0.14
Losses.		0.5			1.03	0.06

TABLE 12

Dehydrogenation of the Paraffin-Naphthene Part VT-2

Amt. of Fraction VT-2 (g)	Amount of Fraction GT-2 obtained: actually (g)	corr. (g)	% in VT-2	% in TsT-2	Hydrogen and losses: (g)	% in VT-2	% in TsT-2
708.0	688.0	688.4	97.23	73.32	19.6	2.77	2.09

Separation of the catalyzate GT-2 into aromatic hydrocarbons and a mixture of paraffins and cyclopentanes. The catalyzate GT-2 was subjected to chromatographic adsorption analysis and was separated into aromatics DT-2 formed by the dehydrogenation of cyclohexane hydrocarbons, and the paraffin-cyclopentane fraction ET-2. The catalyzate GT-2, containing about 10% of aromatics (as shown by a separate test), was resolved with separation of an intermediate fraction and the subsequent resolution of that with the aid of isopentane. The results of the resolution of the catalyzate GT-2 are given in Table 13.

After removal of isopentane, the separated fractions, DT-2 and ET-2, had the following properties:

	n_D^{20}	d_4^{20}	Aniline point (°C)
DT-2.	1.4953	0.8640	–
ET-2	1.3953	0.7028	66.1

Investigation of the aromatics DT-2. The aromatic hydrocarbons DT-2 were fractionated through a column of about 40-plate efficiency (similarly to the aromatics BT-2). The results of the fractionation, the properties of the fractions, and results of the optical analysis are given in Fig. 4 and Table 14. In the same table are given the results of the recalculation of the amounts of the separated aromatic fractions into the amounts of the corresponding cyclohexane hydrocarbons contained in the original gasoline.

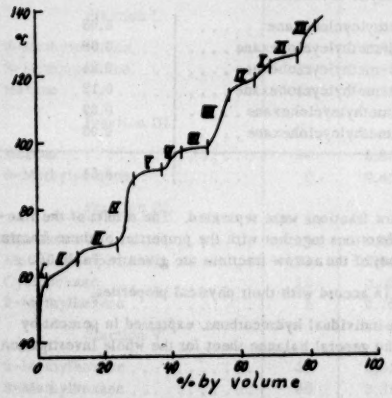

Fig. 5. Fractionation curve of the paraffin-cyclopentane part ET-2.

Investigation of the paraffin-cyclopentane part ET-2. The paraffin-cyclopentane part ET-2 was fractionated through a 50-plate column into narrow fractions. A preliminary determination of the fractionation curve was made with the same column on 100 ml of ET-2. The fractionation was carried out at a reflux number of 45-50 with continuous separation of distillate. The fractionation curve of ET-2 is given in Fig. 5. The vertical lines indicate the limits of the narrow fractions that were later taken; the selection of these limits was determined by the character of the fractionation curve and the boiling points of the individual hydrocarbons.

When the fractionation curve had been determined, 300 ml of ET-2 was fractionated into narrow fractions through the same column with continuous separation of

TABLE 13

Chromatographic Resolution of the Catalyzate GT-2

Amt. of catalyzate GT-2 (g)	Results of separation										
	Aromatics DT-2				Paraffin-cyclopentane part ET-2				Losses		
	actual (g)	corr. (g)	% in GT-2	% in TsT-2	actual (g)	corr. (g)	% in GT-2	% in TsT-2	(g)	% in GT-2	% in TsT-2
667.7	63.1	64.5	9.67	7.09	594.2	594.8	89.08	65.32	8.34	1.25	0.92

TABLE 14

Fractionation of the Aromatics DT-2

Fraction No.	Boiling range in °C (760 mm)	Weight of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction (% by weight in DT-2)	Content of corresponding cyclohexanes in TsT-2 (% by weight)
Amount taken for fractionation		62.75	1.4953	0.8640	100.00	
I	78.0-100.0	7.2	1.4953	0.8673	11.47	0.88
II	100.0-128.1	23.55	1.4941	0.8622	37.53	2.83
III	128.1-150.1	22.45	1.4954	0.8638	35.78	2.68
IV	150.1-162.9	5.25	1.4946	0.8657	8.37	0.62
Residue		1.55			2.47	0.18
Losses		2.75			4.38	0.33

Results of the Optical Analysis of Fraction III

	Content of aromatic hydrocarbons in Fraction III (% by wt.)		Content of corresponding cyclohexane hydrocarbons in TsT-2 (% by wt.)
o-Xylene	17	1,2-Dimethylcyclohexane	0.46
m-Xylene	41	1,3-Dimethylcyclohexane	1.10
p-Xylene	16	1,4-Dimethylcyclohexane	0.43
Ethylbenzene	26	Ethylcyclohexane	0.70
Total	100		2.69

Results of the Optical Analysis of Fraction IV

o-Xylene	5	1,2-Dimethylcyclohexane	0.03
1-Ethyl-2-methylbenzene	15	1-Ethyl-2-methylcyclohexane	0.09
1-Ethyl-3-methylbenzene	40	1-Ethyl-3-methylcyclohexane	0.25
1-Ethyl-4-methylbenzene	20	1-Ethyl-4-methylcyclohexane	0.12
1,2,4-Trimethylbenzene	15	1,2,4-Trimethylcyclohexane	0.09
1,3,5-Trimethylbenzene	5	1,3,5-Trimethylcyclohexane	0.03
Total	100		0.61

distillate, the reflux number being 40-45. In all, fifteen narrow fractions were separated. The results of the fractionation of the paraffin-cyclopentane part ET-2 into narrow fractions together with the properties of these fractions are given in Table 15, and the results of the Raman spectra study of the narrow fractions are given in Table 16.

The results of the optical analysis of these fractions are in accord with their physical properties.

All of the results obtained relating to the contents of the individual hydrocarbons, expressed in percent by weight on the whole gasoline TsT-2, are given in Table 2. The general balance sheet for the whole investigation is given in the same table.

TABLE 15

Fractionation of the Paraffin-Cyclopentane Part ET-2

Fraction No.	Boiling range (°C)	Weight of fraction (g)	Content of fraction (% by wt.) in ET-2	Content of fraction (% by wt.) in TsT-2	n_D^{20}	d_4^{20}	Aniline point (°C)
Amt. taken for fractionation		211.4	100.00	65.32	1.3953	0.7028	66.1
I	33.9- 58.0	4.5	2.13	1.39	1.3689	0.6502	62.9
II	58.0- 65.0	19.3	9.13	5.96	1.3735	0.6580	71.4
III	65.0- 70.0	23.4	11.07	7.23	1.3772	0.6656	66.5
IV	70.0- 89.0	10.5	4.97	3.25	1.3963	0.7120	50.7
V	89.0- 92.5	21.4	10.12	6.61	1.3945	0.7037	63.5
VI	92.5- 98.0	8.0	3.78	2.47	1.3925	0.6977	65.1
VII	98.0- 99.0	17.2	8.14	5.32	1.3893	0.6874	67.8
VIII	99.0-115.5	15.5	7.33	4.79	1.4033	0.7233	61.8
IX	115.5-119.0	17.3	8.18	5.34	1.4018	0.7150	68.7
X	119.0-124.0	8.1	3.83	2.50	1.4045	0.7223	65.7
XI	124.0-126.0	14.1	6.67	4.36	1.4005	0.7113	69.0
XII	126.0-134.0	10.2	4.82	3.15	1.4044	0.7209	68.4
XIII	134.0-138.0	9.3	4.40	2.87	1.4145	0.7438	67.2
XIV	138.0-144.5	12.8	6.05	3.95	1.4128	0.7382	69.2
XV	144.5-149.6	7.8	3.69	2.41	1.4110	0.7336	70.5
Residue		7.0	3.31	2.16			
Losses		5.0	2.38	1.56			

TABLE 16

Results of the Optical Investigation of Narrow Fractions of the Paraffin-Cyclopentane Part ET-2

Hydrocarbons found by the optical method	Content of hydrocarbons (% by wt.) in the fraction	Content of hydrocarbons (% by wt.) in TsT-2	Hydrocarbons found by the optical method	Content of hydrocarbons (% by wt.) in the fraction	Content of hydrocarbons (% by wt.) in TsT-2
1	2	3	4	5	6
Fraction I			Fraction VI		
Pentane	60	0.83	3-Methylhexane	5	0.12
Cyclopentane	15	0.21	trans-1,2-Dimethylcyclopentane	15	0.37
2,2-Dimethylbutane	5	0.07	Heptane	80	1.98
2-Methylpentane	20	0.28	Fraction VII		
Fraction II			Heptane	100	5.32
2-Methylpentane	45	2.68	Fraction VIII		
3-Methylpentane	33	1.97	Heptane	51	2.44
Hexane	22	1.31	cis-1,2-Dimethylcyclopentane	10	0.48
Fraction III			Methylcyclohexane	19	0.91
Hexane	94	6.80	Ethylcyclopentane	15	0.72
3-Methylpentane	6	0.43	2-Methylheptane	5	0.24
Fraction IV			Fraction IX		
Hexane	10	0.32	2-Methylheptane	60	3.20
Methylcyclopentane	75	2.44	3-Methylheptane	25	1.34
Cyclohexane	10	0.33	4-Methylheptane	15	0.80
2-Methylhexane	5	0.16	Fraction X		
Fraction V			2-Methylheptane	50	1.25
2-Methylhexane	35	2.31	3-Methylheptane	15	0.37
3-Methylhexane	50	3.31	1,1-Dimethylcyclohexane	5	0.13
trans-1,2-Dimethylcyclopentane	15	0.99	Octane	30	0.75

TABLE 16 (Continued)

1	2	3	4	5	6
Fraction XI			Not accounted for	45	1.29
Octane	94	4.10	Fraction XIV		
Not accounted for	6	0.26	1,1,3-Trimethylcyclohexane	~20	0.79
Fraction XII			4-Methyloctane	40	1.58
Octane	72	2.27	3-Methyloctane	30	1.18
1,1,3-Trimethylcyclohexane	28	0.88	Not accounted for	10	0.40
Fraction XIII			Fraction XV		
1,1,3-Trimethylcyclohexane	~35	1.01	Nonane	85	2.05
4-Methyloctane	20	0.57	Not accounted for	15	0.36

The laboratory assistants, T. V. Lapshina, V. A. Ovodova, K. G. Ryabova, and G. S. Taits, took part in this investigation.

SUMMARY

1. By the aid of the combination method of investigating the individual hydrocarbon composition of straight-run gasolines, the analysis has been carried out of a gasoline having an upper boiling limit of 150° derived from a sample of a low-sulfur Tuimazin petroleum (Devonian level).

2. The individual hydrocarbon composition of the Tuimazin gasoline has been accounted for quantitatively to the extent of 87.9% (by weight on the whole gasoline). The total losses were about 6%.

3. It has been found that normal paraffins predominate in this essentially paraffin gasoline from Tuimazin petroleum. Among the cyclopentanes, methylcyclopentane is present in the greatest amount. Among the cyclohexanes, methyl-, 1,3-dimethyl-, and 1,1,3-trimethyl-cyclohexanes are present in the greatest amounts. Among the aromatic hydrocarbons, toluene and m-xylene are present in the greatest amounts.

Received July 20, 1953

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COMPLEX COMPOUNDS OF METAL HALIDES WITH ALCOHOLS

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In connection with some investigations that we are carrying out on the alkylation of aromatic compounds with alcohols in presence of $ZnCl_2$ and other metal chlorides, we have studied the reactions of metal halides ($ZnCl_2$, $ZnBr_2$, $AlCl_3$, $CdCl_2$, $MgCl_2$ and $CaCl_2$) with various alcohols (cyclohexanol, menthol, isopropyl alcohol, 2-methyl-2-butanol, and 1,1-dimethylethanol). Only a few papers have appeared that describe the preparation and properties of compounds of metal halides with various alcohols. These compounds have been regarded as analogs of the crystal hydrates of salts, and have therefore been termed crystal alcoholates [1].

The first compounds of this class were prepared as long ago as 1827. The compounds then obtained were those formed by $CaCl_2$ with methyl and ethyl alcohols. Later compounds containing other metals were described, for example, compounds of $CaCl_2$ [2], $MgCl_2$, $MgBr_2$, and LiCl [3], $SrBr_2$ [4], and NaI [5].

Menshutkin [6] made a detailed study of the compounds formed by $MgBr_2$, MgI_2, and $CaCl_2$ with various alcohols and ethers. He established that these compounds vary in composition according to the conditions under which the reaction is carried out: $CaCl_2$ gives a compound of the type $CaCl_2 \cdot 4ROH$ at below 55°, and of the type $CaCl_2 \cdot 3ROH$ at above this temperature. He studied also the compounds formed by phenol and by phenetole with $SbCl_3$, and isolated $2SbCl_3 \cdot C_6H_5OH$ and $SbCl_3 \cdot C_6H_5OC_2H_5$ [7]. Compounds of alcohols with boron trifluoride and aluminum chloride are also known. Boron trifluoride [8] will unite both with one and with two molecules of alcohol. According to the conditions, aluminum chloride [9] reacts with alcohols in two directions: in the cold crystalline addition products of the type $Al_2Cl_6 \cdot nROH$ are formed, and at higher temperatures with excess of $AlCl_3$ substitution products of the type $Al_2Cl_4(OR)_2$ are obtained.

Tsukervanik [10] made a detailed study of the reaction of isobutyl alcohol with $AlCl_3$, and he obtained the crystalline partial alkoxide $AlCl_2O \cdot C_4H_9$-i; investigations on the compounds of $FeCl_3$ with alcohols [11] find their place here. Molecular compounds of alcohols with other metal chlorides are also described in the literature [12].

We have prepared a compound of cyclohexanol and zinc bromide by a method described previously [13]; it contains two molecules of cyclohexanol and one of zinc bromide, and is a crystalline substance, readily soluble in organic solvents. The benzene and acetone solutions of this substance have acidic properties; when it is heated with phenol, p-cyclohexylphenol is formed; with acetic acid it gives cyclohexyl acetate.

The compound of aluminum chloride and cyclohexanol was prepared by reaction in the cold between the component substances in petroleum ether (b.p. 48-50°) solution. The white crystalline substance $AlCl_3 \cdot 6C_6H_{11}OH$; was formed. This substance is very hygroscopic, and it dissolves in organic solvents. Its benzene, alcohol, and acetone solutions show acid reactions to indicators (Methyl orange, phenylazo-1-naphthylamine, Dimethyl Yellow).

A solution prepared from $AlCl_3 \cdot 6C_6H_{11}OH$ and cyclohexanol was found to be electrically conducting. For 0.02 M $AlCl_3 \cdot C_6H_{11}OH$ in cyclohexanol $\lambda_m = 2.40$; and for 0.01 M $\lambda_m = 1.20$ (20°). This compound is decomposed by heat with formation of cyclohexanol, cyclohexene, chlorocyclohexane, HCl, and other substances. Long heating of $AlCl_3 \cdot 6C_6H_{11}OH$ (water bath) in petroleum ether solution until evolution of HCl ceases leads to the formation of a crystalline substance corresponding in composition to $C_6H_{11}OAlCl_2 \cdot 5C_6H_{11}OH$. A solution of this substance in benzene has acidic properties. At 150-200° it decomposes to cyclohexanol, cyclohexene, chlorocyclohexene, and $AlCl_2OH$.

On the basis of the results described above and in the literature [14], the reaction of $AlCl_3$ with cyclohexanol may be represented by the following scheme:

$$AlCl_3 + 6C_6H_{11}OH \longrightarrow AlCl_3 \cdot 6C_6H_{11}OH. \quad (1)$$

$$AlCl_3 \cdot 6C_6H_{11}OH \longrightarrow C_6H_{11}OAlCl_2 \cdot 5C_6H_{11}OH + HCl. \quad (2)$$

$$C_6H_{11}OAlCl_2 \cdot 5C_6H_{11}OH \longrightarrow C_6H_{10} + 5C_6H_{11}OH + AlCl_2OH. \quad (3)$$

$$C_6H_{10} + HCl \longrightarrow C_6H_{11}Cl. \quad (4)$$

Menthol and zinc chloride form the crystalline compound $C_{10}H_{19}OH \cdot ZnCl_2$. This is decomposed by heat

into menthene, $ZnCl_2$, and water. It is readily soluble in organic solvents.

In order to compare the complex compounds of zinc and aluminum halides with other analogous compounds, we have studied also the complexes formed by cadmium, calcium, and magnesium chlorides with various alcohols. At 130° calcium chloride and cyclohexanol form a white crystalline substance, corresponding in composition to the formula $CaCl_2 \cdot 3C_6H_{11}OH$. It is decomposed by heat into $CaCl_2$ and cyclohexanol, no cyclohexene formation being observed. An attempt to effect its condensation with phenol did not lead to the formation of p-cyclohexylphenol [distinction from $(C_6H_{11}OH)_2 \cdot ZnBr_2$]. This compound is difficultly soluble in organic solvents; its benzene solution gives a weakly acid reaction to phenylazo-1-naphthylamine.

With cyclohexanol and 2-methyl-2-butanol, magnesium chloride gives crystalline compounds having the compositions $MgCl_2 \cdot 3C_6H_{11}OH$ and $MgCl_2 \cdot 3C_5H_{11}OH$ (tert.). The second compound, when heated in a water bath with glacial acetic acid, reacts with formation of 1,1-dimethylpropyl acetate. When heated, both compounds decompose into $MgCl_2$ and the corresponding alcohol.

Cadmium chloride readily reacts with cyclohexanol and with isopropyl alcohol, the crystalline substances $CdCl_2 \cdot C_6H_{11}OH$ and $CdCl_2 \cdot C_3H_7OH$-i being formed. These are almost insoluble in organic solvents and do not have acidic properties. When heated, they decompose with formation of the corresponding alcohols and $CdCl_2$.

We then studied the reactions of 2-methyl-2-butanol and 1,1-dimethylethanol with $ZnCl_2$ and $ZnBr_2$. We isolated crystalline compounds consisting of two molecules of alcohol and one of zinc halide. These compounds are all very hygroscopic. They are readily soluble in organic solvents, and their solutions in benzene have acidic properties. When heated, they readily decompose with formation of olefins, the corresponding metal halides, and water. When the compound of $ZnBr_2$ with $C_5H_{11}OH$ (tert.) is heated with phenol, p-(1,1-dimethylpropyl) phenol is formed; with acetic acid, 1,1-dimethylpropyl acetate is formed.

On the basis of the facts given above we consider that the compounds formed by the metal halides studied with alcohols can be differentiated as follows, according to their behavior.

1. The compounds formed by $CaCl_2$, $MgCl_2$ and $CdCl_2$ with alcohols, unlike the analogous compounds of $ZnCl_2$, $ZnBr_2$ and $AlCl_3$ are decomposed by heat into the corresponding alcohols and metal halides. They are difficultly soluble in organic solvents, and their solutions have only very weakly acid properties ($CaCl_2$ compounds), or are completely devoid of such properties ($CdCl_2$ and $MgCl_2$ compounds). We consider that these compounds are typical crystal alcoholates.

2. The compounds formed by $ZnCl_2$, $ZnBr_2$ and $AlCl_3$ with alcohols are different in character. They have more strongly marked acid properties than compounds of the first group, and they have definite melting points. Also, at temperatures above their melting points they decompose with formation of new compounds (C_nH_{2n}, RX, ROH, H_2O and others). This indicates that the linkage between $ZnCl_2$, $ZnBr_2$, $AlCl_3$ and alcohols is stronger than in compounds formed by the metal halides of the first group (Cd, Ca, Mg). It is by this difference in the properties of the halogen compounds of Zn and Al on the one hand and of Ca, Mg, and Cd on the other that the behavior of metal halides in the alkylation reactions of alcohols with aromatic compounds can be explained.

On the basis of our results and of those described in the literature it must be supposed that the compositions of the complex compounds formed by metal halides with alcohols depend on the reaction conditions and the chemical nature of the metal halides. For example, for Zn halide compounds with two molecules of alcohol are characteristic; for Al those with six, for Cd those with one, and for Ca and Mg those with three.

Also, in order to determine whether complex-formation may occur between Zn halides and olefins, we have studied the action of 2-methyl-2-butene and hexene isomers (a mixture of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene) on zinc bromide. It was found that zinc bromide reacts with these olefins in presence of moisture. Crystalline compounds of the following composition were obtained: $(C_5H_{10})_2 \cdot ZnBr_2 \cdot 2H_2O$ and $C_6H_{12} \cdot 2ZnBr_2 \cdot H_2O$.

These compounds are very hygroscopic, and they have acidic properties. They are decomposed by water into the corresponding alcohols and zinc bromide. With phenol, alkylphenols are formed. They enter into an esterification reaction with acetic acid with formation of esters. Kondakov [15], together with other complex compounds of zinc chloride, described for the first time the complex formed from 2-methyl-2-butene and zinc chloride, which had the composition $C_5H_{10} \cdot 2ZnCl_2 \cdot H_2O$. We have repeated Kondakov's experiments with 2-methyl-2-butene and zinc chloride, and we have succeeded in isolating this complex, which was found to have acidic properties and to enter into the esterification reaction with organic acids and the alkylation reaction with phenol.

EXPERIMENTAL

Starting Materials. Anhydrous metal halides were prepared from commercial products as indicated in the literature [15]. The alcohols were made absolute by a previously described method [13]. The reactions were carried out in a small round-bottomed flask fitted with reflux condenser protected by a calcium chloride tube.

Cyclohexanol and Zinc Bromide. A mixture of 30 g (0.3 mole) of cyclohexanol and 22.4 g (0.1 mole) of zinc bromide was heated in an oil bath for six hours. The reaction mixture was then treated with a mixture of petroleum ether and diethyl ether, when white needles were precipitated. They melted at 74-76° and were very hygroscopic; they dissolved readily in benzene, ether, acetone, and alcohol, but not readily in petroleum ether. A benzene solution of this substance gave an acid reaction with various indicators (phenylazo-1-naphthylamine, Methyl orange, Dimethyl Yellow). When the complex was heated at above 140°, it decomposed into cyclohexene, $ZnBr_2$, and water.

	Found %:	Br 37.83
$ZnBr_2 \cdot 2C_6H_{11}OH$.	Calculated %:	Br 37.64
	Found:	M 415 (cryoscopically in benzene solution)
$ZnBr_2 \cdot 2C_6H_{11}OH$.	Calculated:	M 425

Phenol and $ZnBr_2 \cdot 2C_6H_{11}OH$. A mixture of 14 g (0.15 mole) of phenol and 10.5 g (0.025 mole) of $ZnBr_2 \cdot 2C_6H_{11}OH$ was heated at 145-150° for four hours. The contents of the flask were then decomposed with cold acidified water. The organic part was separated, and the lower, aqueous layer was extracted twice with a small amount of benzene. The benzene extracts were united to the organic part, which was then washed, dried with $CaCl_2$, and fractionated, two fractions being obtained:

Fraction I, b.p. 180-240°; 9.3 g
Fraction II, b.p. 240-300°; 7.2 g

When Fraction II was allowed to stand, crystals of p-cyclohexylphenol separated. The liquid part of Fraction II, after removal of the crystals, was united with Fraction I, which was then treated with 15% NaOH solution. The alkaline solution was neutralized with dilute HCl, and the substance that then separated was washed, dried with $CaCl_2$, and fractionated. Altogether, 5.1 g (60%) of p-cyclohexylphenol was obtained; the by-products (phenol ethers) were not studied.

p-Cyclohexylphenol [16] was obtained as white crystals, m.p. 128-129° (from benzene).

Found %:	C 81.82; H 9.42
$C_{12}H_{16}O$. Calculated %:	C 81.76; H 9.16

Acetic Acid and $ZnBr_2 \cdot 2C_6H_{11}OH$. A mixture of 4 g (0.06 mole) of CH_3COOH and 8.5 g (0.02 mole) of $ZnBr_2 \cdot 2C_6H_{11}OH$, was heated at 100-120° for ten hours. Suitable treatment and fractionation of the reaction product yielded 2.5 g (44%) of cyclohexyl acetate, a liquid of b.p. 172-174°; d_{25}^{20} 0.9685; n_D^{20} 1.4430; found MR 38.58; calculated at $C_8H_{14}O_2$ MR 38.60.

Reaction Product from Cyclohexanol and Aluminum Chloride. The substances taken were cyclohexanol (20 g, i.e. 0.2 mole), aluminum chloride, (2.5 g, i.e. 0.016 mole), and petroleum ether (15 ml). The reaction was carried out in the cold with vigorous stirring. The aluminum chloride was added slowly (over a period of ten hours) to a solution of the cyclohexanol in the petroleum ether. During the reaction no evolution of hydrogen chloride was to be noted. When reaction was complete, the mass was left overnight. White crystals came down, and these were filtered off, washed with petroleum ether (b.p. 45-50°), pressed off, and dried in nitrogen in a desiccator over P_2O_5. The total amount of product obtained was 12 g (84%). The complex obtained melted at 60-65° with decomposition, and was soluble in benzene, alcohol, acetone, and ether, but difficultly soluble in petroleum ether; its benzene solution gave an acid reaction to various indicators (Methyl orange, phenylazo-1-naphthylamine). Analysis for carbon, hydrogen, aluminum, and chlorine indicated the formation of a compound of the composition $AlCl_3 \cdot 6C_6H_{11}OH$.

Found %:	C 58.43; H 9.51; Cl 14.35; Al 3.48
$AlCl_3 \cdot 6C_6H_{12}O$. Calculated %:	C 58.91; H 9.81; Cl 14.50; Al 3.67

When $AlCl_3 \cdot 6C_6H_{11}OH$ was heated to 150-200°, it decomposed with formation of cyclohexene, chlorocyclohexane, cyclohexanol, and hydrogen chloride. When a petroleum ether solution of $AlCl_3 \cdot 6C_6H_{11}OH$ was heated in a water bath under reflux until, after a considerable time, the evolution of HCl ceased, a crystalline

substance melting with decomposition at 50-55° was formed. On the basis of analysis for chlorine and aluminum it may be supposed that this substance had the composition $AlCl_2OC_6H_{11} \cdot 5C_6H_{11}OH$.

Found %: Al 3.97; Cl 10.44

$AlCl_2OC_6H_{11} \cdot 5C_6H_{12}O$. Calculated %: Al 3.87; Cl 10.17

When $AlCl_2OC_6H_{11} \cdot 5C_6H_{12}O$ was heated at above 150°, cyclohexene, chlorocyclohexane, and cyclohexanol were obtained.

Cyclohexanol and Magnesium Chloride. A mixture of 25 g (0.25 mole) of cyclohexanol and 4.7 g (0.05 mole) of magnesium chloride was heated for ten hours at 125-130°. The product was then filtered off, washed with petroleum ether, and dried in a desiccator over P_2O_5. The substance so obtained consisted of extremely hygroscopic white crystals, which, when heated, decomposed into the original components without melting. The substance was of low solubility in organic solvents (benzene and acetone), apart from alcohol, in which it dissolved readily. Its benzene and acetone solutions gave almost no signs of acid reaction with phenylazo-1-naphthylamine. When heated (water bath) with glacial acetic acid, cyclohexyl acetate was formed. According to analysis the compound had the composition $MgCl_2 \cdot 3C_6H_{11}OH$.

Found %: Cl 17.40; Mg 6.50

$MgCl_2 \cdot 3C_6H_{12}O$. Calculated %: Cl 17.72; Mg 6.15.

2-Methyl-2-butanol and Magnesium Chloride. A mixture of 9 g (0.1 mole) of 2-methyl-2-butanol and 1.2 g (0.05 mole) of magnesium chloride was heated at 100-110° for six hours. The resulting crystalline substance (white needles) was filtered off, washed with petroleum ether, and dried in a desiccator over P_2O_5. It was found to be of low solubility in benzene, ether, and acetone, but readily soluble in alcohol. When heated, it decomposed without melting into magnesium chloride and the original alcohol. It had no acidic properties. When it was heated with phenol at 140°, no (1,1-dimethylpropyl) phenol was formed .

Found %: Cl 20.17

$MgCl_2 \cdot 3C_5H_{11}OH$. Calculated %: Cl 19.77

Cyclohexanol and Calcium Chloride. A mixture of 30 g (0.3 mole) of cyclohexanol and 5.5 g (0.05 mole) of calcium chloride was heated at 120-130° for six hours. After suitable treatment the resulting white crystals were dried over P_2O_5 in a desiccator. This substance was found to be soluble in alcohol and acetone, but difficultly soluble in benzene and petroleum ether. Its benzene solution gave a very feeble acid reaction to phenylazo-1-naphthylamine. When heated, it decomposed into $CaCl_2$ and the original cyclohexanol. The compound obtained had the composition $CaCl_2 \cdot 3C_6H_{11}OH$.

Found %: C 52.00; H 9.35; Cl 16.88; Ca 9.80

$CaCl_2 \cdot 3C_6H_{12}O$. Calculated %: C 52.55; H 8.75; Cl 17.0; Ca 9.75

Cyclohexanol and Cadmium Chloride. A mixture of 20 g (0.3 mole) of cyclohexanol and 5.6 g (0.05 mole) of cadmium chloride was heated at 125-130° for eight hours. The white crystalline substance obtained was very hygroscopic and was difficultly soluble in benzene, acetone, and petroleum ether; it readily dissolved in alcohol. The substance was found to have very feeble acidic properties. When heated, it decomposed into $CdCl_2$ and the original cyclohexanol.

Found %: C 25.46; 25.47; H 4.06; 4.05; Cl 25.49; 25.28

$CdCl_2 \cdot C_6H_{12}O$. Calculated %: C 25.40; H 4.24; Cl 25.03

Isopropyl Alcohol and Cadmium Chloride. A mixture of 12 g (0.2 mole) of isopropyl alcohol and 9 g (0.1 mole) of cadmium chloride was heated at 110-120° for five hours. A crystalline substance was formed and was found to be of low solubility in many organic solvents (benzene, toluene, acetone, and ether), but readily soluble in alcohols. When heated, this substance decomposed without melting into $CdCl_2$ and the original isopropyl alcohol.

Found %: Cl 28.80

$CdCl_2 \cdot C_3H_7OH$. Calculated %: Cl 29.00

(−)-Menthol and Zinc Chloride. A mixture of 7.1 g (0.05 mole) of menthol and 3.0 g (0.022 mole) of zinc chloride was heated at 100-110° for eight hours. The resulting white needles were soluble in many organic solvents (benzene, alcohol, acetone, ether), but difficultly soluble in petroleum ether. A benzene solution of the substance was found to have acid properties. It melted with decomposition at 103-105°.

Found %: Cl 24.66

$ZnCl_2 \cdot C_{12}H_{19}OH$. Calculated %: Cl 24.42

1,1-Dimethylethanol and Zinc Chloride. A mixture of 15 g (0.2 mole) of 1,1-dimethylethanol and 6.8 g (0.05 mole) of zinc chloride was sealed in a glass tube and set aside at room temperature for 25 days. White crystals (prisms) formed in the reaction mixture, and were filtered off, washed with petroleum ether, and dried over P_2O_5. The resulting crystals were very hygroscopic and readily became liquid when exposed to the atmosphere. They were readily soluble in benzene, ether, acetone, and alcohols, but difficultly soluble in petroleum ether, pentane, and hexane. The benzene solution of this complex had acidic properties. The melting point of the substance was 56-58°.

Found %: Cl 24.92

$ZnCl_2 \cdot 2C_4H_{10}O$. Calculated %: Cl 25.00

Found: M 278.7

$ZnCl_2 \cdot 2C_4H_{10}O$. Calculated: M 284.4

When the substance was heated (water bath) with glacial acetic acid, tert-butyl acetate was formed.

Alkylation of Phenol by the Complex $ZnCl_2 \cdot 2C_4H_9OH$ (Tert). A mixture of 2.84 g (0.01 mole) of $ZnCl_2 \cdot 2C_4H_9OH$ and 9.4 g (0.1 mole) of phenol was heated in a water bath for six hours. Suitable treatment of the reaction product yielded 15 g of p-tert-butylphenol (m.p. 98-99°).

Found %: C 79.81; H 9.12

$C_{10}H_{14}O$. Calculated %: C 80.00; H 9.33

2-Methyl-2-butanol and Zinc Chloride. A mixture of 22 g (0.25 mole) 2-methyl-2-butanol and 13.6 g (0.1 mole) zinc chloride was stored in a sealed tube for 45 days* when white crystals (prisms) had appeared. These were filtered off, washed with petroleum ether, and dried over P_2O_5. The substance so obtained, which melted at 62-64°, was very hygroscopic and of good solubility in organic solvents. Its benzene solutions had acidic properties. With glacial acetic acid it yielded 1,1-dimethylpropyl acetate.

Found %: Cl 22.45

$ZnCl_2 \cdot 2C_5H_{12}O$. Calculated %: Cl 22.74

Found: M 304

$ZnCl_2 \cdot 2C_5H_{12}O$. Calculated: M 312

Alkylation of Phenol by the Complex $ZnCl_2 \cdot 2C_5H_{11}OH$ (tert). A mixture of 3 g (0.01 mole) of $ZnCl_2 \cdot 2C_5H_{11}OH$ and 9.4 g (0.1 mole) of C_6H_5OH was heated in a water bath for six hours. The product was 1.5 g of p-(1,1-dimethylpropyl) phenol, m.p. 91-92°.

2-Methyl-2-butanol and Zinc Bromide. Reaction between 22 g (0.25 mole) of 2-methyl-2-butanol and 11.25 g (0.05 mole) of zinc bromide yielded a crystalline substance (prisms) which readily became liquid when exposed to the atmosphere. The crystals were readily soluble in many organic solvents, but difficultly soluble in petroleum ether; they melted at 60-62°. When heated with acetic acid, they yielded 1,1-dimethylpropyl acetate, and when heated with phenol they gave p-(1,1-dimethylpropyl) phenol.

Found %: Br 40.24; 39.86

$ZnBr_2 \cdot 2C_5H_{12}O$. Calculated %: Br 40.00

Found: M 393.6

$ZnBr_2 \cdot 2C_5H_{12}O$. Calculated: M 401.2

1,1-Dimethylethanol and Zinc Bromide. Reaction between 15 g (0.2 Mole) of 1,1-dimethylethanol and 11.25 g (0.05 mole) of zinc bromide yielded prisms of m.p. 53-55°. They were readily soluble in benzene, toluene, and alcohol, but of poor solubility in hydrocarbons of the aliphatic series. Water decomposed them with formation of the alcohol (C_4H_9OH). The benzene solutions of the substance were found to have acidic properties. The complex was found to take part in esterification reactions with organic acids (CH_3COOH).

Found %: Br 42.15

$ZnBr_2 \cdot 2C_4H_{10}O$. Calculated %: Br 42.87

2-Methyl-2-butene and Zinc Bromide. A mixture of 7 g (0.1 mole) of 2-methyl-2-butene and 24 g of moist zinc bromide was set aside in a sealed tube for a long period of time (ten months). The tube was then

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* At room temperature.

opened, and the white crystals that had formed (needles, m.p. 60-62°) were filtered off, washed with pentane, and dried over P_2O_5 in a vacuum desiccator. The resulting substance was very hygroscopic; it was readily soluble in many organic solvents, but difficultly soluble in hydrocarbons (pentane, hexane, petroleum ether). Its benzene solutions gave an acid reaction to phenylazo-1-naphthylamine. When treated with water, the substance was decomposed into 2-methyl-2-butanol and zinc bromide. When a mixture of it with phenol was heated (water bath), (1,1-dimethylpropyl) phenol was formed. With acetic acid under the same conditions it yielded 1,1-dimethylpropyl acetate. Analyses of this substance indicated the composition $(C_5H_{10})_2 \cdot ZnBr_2 \cdot 2H_2O$.

Found %: C 29.11; 28.93; H 6.04; 5.91; Br 40.25; 40.15

$(C_5H_{10})_2 \cdot ZnBr_2 \cdot 2H_2O$. Calculated %: C 29.92; H 5.95; Br 39.91

Hexene Isomers and Zinc Bromide. A mixture of 24 g of $ZnBr_2$ and 7 g of a moist mixture of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene was set aside in a sealed tube at room temperature for six months. The crystals (prisms) that had formed in the course of this time were separated from liquid, washed, and dried in a desiccator over P_2O_5. The resulting crystals were very hygroscopic, were readily soluble in benzene, alcohol and acetone, and had acidic properties. Water decomposed the complex with formation of 2,3-dimethyl-2-butanol. Analyses indicated that the compound had the formula $C_6H_{12} \cdot 2ZnBr_2 \cdot H_2O$.

Found %: C 13.21; H 2.71; Br 58.07

$C_6H_{12} \cdot 2ZnBr_2 \cdot H_2O$. Calculated %: C 13.04; H 2.53; Br 57.86

SUMMARY

1. It has been shown that, when the halides of certain metals of the second and third groups of Mendeleev's system ($ZnCl_2$, $ZnBr_2$, $AlCl_3$, $CaCl_2$, $MgCl_2$ and $CdCl_2$) react with aliphatic (isopropyl alcohol, 1,1-dimethylethanol, 2-methyl-2-butanol) and cyclic (cyclohexanol, menthol) alcohols, crystalline complex compounds of an acidic nature are formed. In this reaction, zinc halides unite with two alcohol molecules, aluminum halides with six, calcium and magnesium with three, and cadmium with one.

2. When heated, the complexes formed with $ZnCl_2$, $ZnBr_2$, and $AlCl_3$, unlike those formed with $MgCl_2$, $CaCl_2$, and $CdCl_2$, break down with formation of new substances (C_nH_{2n}, RX, ROH, MeX_2, H_2O, etc.). The compounds of $MgCl_2$, $CdCl_2$, and $CaCl_2$ with alcohols decompose into the original components under these conditions.

3. When these metal halide complexes are treated with organic acids (CH_3COOH and others), esters are formed.

4. In presence of moisture 2-methyl-2-butene, 2,3-dimethyl-1-butene, and 2,3-dimethyl-2-butene react with zinc bromide with formation of crystalline compounds of composition $(C_5H_{10})_2 \cdot ZnBr_2 \cdot 2H_2O$ and $C_6H_{12} \cdot 2ZnBr_2 \cdot H_2O$.

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Received June 26, 1953

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REACTIONS OF CYCLOHEXENE AT ALUMINOSILICATE CATALYSTS OF DIFFERENT ALUMINA AND SILICA CONTENTS UNDER CONDITIONS PRECLUDING CRACKING. SELECTIVE POISONING BY SODIUM IONS

K. V. Topchieva, A. P. Ballod, I. V. Patsevich, and I. Ptishcheva

In this paper we describe preliminary results of a study of the mechanism of the catalytic action of aluminosilicates on the polymerization and "skeleton" isomerization of hydrocarbons. We were interested in the question of whether polymerization and skeleton isomerization proceeds at the "acidic" active centers associated with cracking and hydrogen redistribution,* or at the active centers of the aluminum oxide.

In the solution of this question we were guided by the following considerations. The relation between the catalytic activity of aluminosilicates and their composition (the ratio Al_2O_3:SiO_2) is described for cracking and hydrogen redistribution by a curve having a maximum at 30% by weight of Al_2O_3 and 70% by weight of SiO_2 [1-7]. An analogous relationship is known between the acidity of aluminosilicates and the Al_2O_3:SiO_2 ratio [6, 8]. "Acidic" active centers are poisoned (cracking) as a result of the exchange adsorption of sodium ions [7, 9]. These facts are to be explained on the basis of the relationship between the catalytic activity of aluminosilicates and their chemical properties, particularly acidity, and the cracking and hydrogen-redistribution centers are to be regarded as equivalent to an aluminosilicic acid, the hydrogen of which participates in the transfer of hydrocarbon hydrogen during the catalytic reaction [7].

For any reaction that is accelerated by aluminosilicates, a study of the dependence of its rate on the Al_2O_3:SiO_2 ratio in the catalyst and on the sodium ion concentration on the catalyst surface permits an approach to be made to the solution of the question of the nature of the active centers in this reaction. We have, therefore, studied polymerization and skeleton isomerization in presence of 1) aluminosilicates of different alumina and silica contents, and 2) aluminosilicates poisoned with respect to cracking and hydrogen redistribution by sodium ions.

As a subject for investigation we selected cyclohexene, which, at temperatures below that at which cracking begins, undergoes polymerization, skeleton isomerization, and hydrogen redistribution. The last reaction has been studied previously only in the case of unsaturated cracking gasoline [1]. We hoped to obtain some supplementary results on this reaction. In previous papers descriptions have been given of the method of preparation [1] and the adsorption properties [2, 5, 10] of the investigated catalysts, and also of the kinetics of the transformations of various hydrocarbons [1, 2, 3, 5, 11] in the presence of these catalysts.

Already in 1950 we established that treatment of an aluminosilicate catalyst with a solution of sodium chloride or carbonate selectively poisons the active centers: whereas activity for the cracking of cumene falls sharply, activity for the dehydration of ethanol is preserved. Adsorption of sodium ions does not appreciably affect the specific surface or the pore distribution [9]. We have established also that aluminum oxide that is active for dehydration does not adsorb Na ions from aqueous salt solutions and does not alter in catalytic activity for dehydration after treatment with a solution of sodium acetate.

Zelinsky and Arbuzov [12] investigated the transformations of cyclohexene at 400° in presence of aluminum oxide containing some silica gel, and they showed that the hydrogenated monomer fraction of the catalyzate consisted of methylcyclopentane. Nikolaeva, Tatevsky, and Frost [13] found that the monomer fraction of the transformation products of cyclohexene, which was passed over natural aluminosilicate at 260°, consisted of saturated and unsaturated hydrocarbons (methylcyclopentane, cyclohexane, methylcyclopentene, and cyclohexene). Petrov and Shchekin [14, 15] investigated the same reaction at 260° and 316° in presence of synthetic aluminosilicate and, while confirming the results of the previous investigators, showed that the polymer fraction consisted mainly of bicyclic hydrocarbons having one five- and one six-membered ring. The authors pointed out the absence of benzene among the light products and of cyclic hydrocarbons having two six- or two five-membered rings among the polymeric products. They suggested that isomerization in presence of aluminosilicates proceeds via depolymerization of an isomerized polymer of cyclohexene.

* Saturation of unsaturated hydrocarbons by redistribution of hydrogen.

EXPERIMENTAL

Cyclohexene, which was prepared by the dehydration of cyclohexanol (b.p. 158.5-159° (760 mm)) over phosphoric acid, had the following constants after being dried and then distilled through a 20-plate column: b.p. 82.5-83° (760 mm); n_D^{20} 1.4466; d_4^{20} 0.8090; iodine number 307.

The reaction was carried out at 350° (no cracking occurs at this temperature) in a continuous-flow apparatus. The monomer fraction (up to 85°) was distilled off from the catalyzate through a 10-plate column. The extent to which polymerization of cyclohexene occurred was determined from the yield of residue after the removal of the monomer fraction. The extent of hydrogen redistribution was determined from the iodine number of the monomer fraction. In order to determine the composition of the monomer fraction, one-half of it was treated with sulfuric acid (sp.gr. 1.84) to remove unsaturated hydrocarbons, and the other half was hydrogenated. The contents of methylcyclopentane and cyclohexane were determined separately for the hydrogenated and sulfonated parts by a refractive index method.* From the results obtained, the contents of methylcyclopentane, methylcyclopentene, cyclohexane, and cyclohexene in the monomer fraction were calculated. From the total content of five-membered hydrocarbons in the monomer fraction, the extent of the isomerization of cyclohexene was calculated. The method is accurate within 2-3%, calculated on the monomer fraction, and it has been verified by the analysis of artificial mixtures.

In Table 1 we give the results of experiments on the transformations of cyclohexene in presence of catalysts of different alumina and silica contents. The total degree of conversion was determined from the amount of unchanged cyclohexene.

TABLE 1

Temperature 350°; space velocity $\underline{v}$ = 1.2 liter/liter·hr; duration of experiment, 1 hour.

Composition of catalyst (% by wt. Al_2O_3:SiO_2)	Composition of catalyzate (% by weight)		Composition of monomer fraction (% by weight on monomer fraction)				Total degree of conversion (%)
	polymers	monomers	saturated	unsaturated	5-membered	6-membered	
0:100	0	100	0	100	0	100	0
10:90	21	79	10	90	19	81	36
16:84	23	77	12	88	35	65	51
30:70	36	64	41.5	58.5	36	64	57
50:50	33	67	40	60	40	60	61
72:28	30	70	20	80	48	52	62
100:0	0	100	0	100	48	52	48

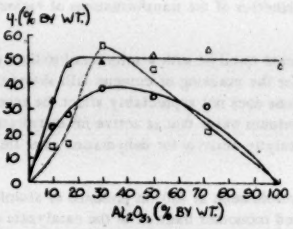

Fig. 1. Dependence of the conversion of cyclohexene on the composition of the aluminosilicate (recalculated to equal weights of samples): Δ = isomerization; o = polymerization; □ = hydrogen redistribution.

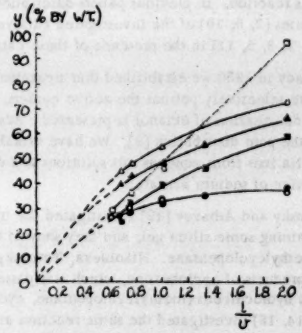

Fig. 2. Dependence of the conversion of cyclohexene on the reciprocal of the space velocity: original sample Δ = isomerization; o = polymerization; □ = hydrogen redistribution; sample containing 29 mg-equiv. of Na per 100 g ▲ = isomerization; ● = polymerization; ■ = hydrogen redistribution.

* Method used by the Kinetics and Catalysis Laboratory of the Petroleum Institute of the USSR Academy of Sciences.

It follows from Table 1 that polymerization and hydrogen redistribution proceed most rapidly in presence of a 30:70 catalyst. For these reactions the variation of activity with change in the composition of the catalyst repeats the results obtained previously for cracking and hydrogen redistribution in gasoline [1-5]. It would appear that the polymerization of cyclohexene proceeds at the same active centers in the aluminosilicate as those at which cracking and hydrogen redistribution occur. Isomerization proceeds differently: the activity of the catalyst for this reaction increases with increase in the alumina content of the catalyst. Pure aluminum oxide is active only for isomerization. The latter was checked at several space velocities (0.5; 0.66; 0.9; 1.2; 1.38; 2.0 liter/liter hr.).

The results given in Table 1 refer to equal apparent bulk volumes of the catalysts, which have different weights, since the bulk specific gravity depends on the Al_2O_3:SiO_2 ratio of the catalyst. In Table 2 and Fig. 1 we give the results of the same experiments after recalculation to equal amounts by weight of the catalysts. The recalculation was made on the basis of kinetic data (the change in yield of the particular substance resulting from change from equal volumes to equal weights was determined from the experimental kinetic curves). This recalculation did not affect the nature of the dependence of the activity of catalysts for polymerization and hydrogen redistribution on the Al_2O_3:SiO_2 ratio, as established from the results in Table 1.

In Table 3 we give the results of the study of the kinetics of the transformation of cyclohexene at a 50:50 aluminosilicate catalyst, pure (the "original"), and poisoned with sodium ions.

TABLE 2

Composition of catalyst (% by wt. Al_2O_3:SiO_2)	Apparent bulk sp.gr.	Space velocity corresponding to equal weights (liter/liter · hour)	Activity (% by weight)			
			for polymerization *	for hydrogen redistribution **	for polymerization **	total degree of conversion
0:100	0.36	0.65	0	0	0	0
10:90	0.44	0.78	23	15	33	55
16:84	0.48	0.86	28	16	48	71
30:70	0.49	0.80	38	56	49	77
50:50	0.57	1.02	35	45	52	71
72:28	0.61	1.11	31	24	54	67
100:0	0.67	1.20	0	0	48	48

* On catalyzate

** On monomer fraction

TABLE 3

Temperature 350°; duration of experiment, 1 hour; 50:50 catalyst, original and containing 29 mg-equiv Na per 100 g

v	1/v	Polymerization*		Hydrogen redistribution**		Isomerization***	
		original catalyst	poisoned catalyst	original catalyst	poisoned catalyst	original catalyst	poisoned catalyst
0.5	2	37	38	97	59	73	67
0.75	1.34	—	35	—	46	—	57
1.0	1.0	33	32	46	39	55	48
1.33	0.75	30	28	36	32	48	43
1.50	0.67	—	26	—	25	45	40
1.66	0.60	27	—	29	—	—	—

* Polymers in catalyzate (%)

** Saturated hydrocarbons in monomer fraction (%)

*** Five-membered hydrocarbons in monomer fraction (%)

The original catalyst (5-6 g) was saturated at room temperature with sodium ions by treatment with 60 ml portions of N sodium acetate for 1-2 days (Miesserov's method [16]).

The amount of adsorbed sodium ions was regarded as equivalent to the acid passing into the solution as a result of the exchange of the acidic hydrogen of the aluminosilicate structure for sodium ions. The acid so formed was determined by titration of the acetate solution with 0.02 N sodium hydroxide to phenolphthalein. It had been previously established that the sodium ion of sodium acetate solution does not replace the hydrogen of the hydroxyl groups of silica gel and alumina gel. The hydrogen ions of the "aluminosilicate" centers were, therefore, removed selectively from the surface. A sample containing 29 mg-equivalents of sodium per 100 g was obtained.

In Fig. 2 the results in Table 3 are presented in the coordinates: degree of conversion (%) and $\frac{1}{v}$ (the value of $\frac{1}{v}$ is proportional to the time of contact).

Polymerization and isomerization on the original and poisoned samples and redistribution on the poisoned sample are described by the equation:

$$v \ln \frac{1}{1-y} = \alpha + \beta v y \qquad (1)$$

which was derived by Frost [17] for unimolecular reactions retarded by the reaction products and occurring in a continuous-flow system. In this equation y is the degree of conversion, α is a constant proportional to the rate constant, v is the space velocity; and β is the retardation constant.

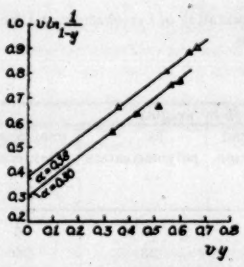

Fig. 3. Kinetics of the isomerization of cyclohexene: ▲ = sample containing 29 mg-equiv. Na per 100 g; △ = original sample.

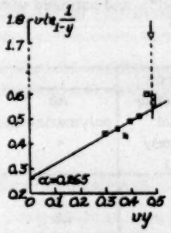

Fig. 4. Kinetics of hydrogen redistribution in the conversion of cyclohexene: □ = original sample; ■ = sample containing 29 mg-equiv. Na per 100 g.

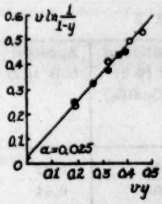

Fig. 5. Kinetics of the polymerization of cyclohexene: ○ = original sample; ● = sample containing 29 mg-equiv. Na per 100 g.

Figures 3, 4, and 5 present the results of a calculation by Frost's equation for the original and poisoned samples. In the calculation, in place of "y" in the equation, the figures in Table 3 have been substituted.

DISCUSSION OF RESULTS

A comparison of the results obtained for the original and poisoned samples shows that the sodium ion, exchange-adsorbed on the catalyst, very greatly reduces its activity for the redistribution of hydrogen. The activity for isomerization is also reduced, but not so greatly as for hydrogen redistribution. The activity for polymerization is identical, within the limits of experimental error, for the original sample and for the sample containing sodium. The value of α, which is proportional to the rate constant, fell as a result of the poisoning from 0.48 to 0.26 for redistribution, and from 0.37 to 0.27 for isomerization. It is noteworthy that the hydrogen-redistribution reaction, which before the poisoning is described by an equation of zero order (vy = const), is described after the poisoning by the equation for a unimolecular reaction retarded by the reaction products (Figs. 2 and 4, and Equation 1).

The results obtained on the redistribution of hydrogen during the transformations of cyclohexene confirm those obtained earlier on the same reaction: 1) the reaction is accelerated only by aluminosilicates, the original oxides, Al_2O_3 and SiO_2 being inactive; and 2) the most active catalyst is that having the ratio of 30:70 [1]. It has been shown for the first time that sodium adsorbed on aluminosilicate poisons it for hydrogen redistribution. These results, taken as a whole, confirm that hydrogen redistribution proceeds at the same "acidic aluminosilicate centers" as cracking does [3, 18].

Isomerization, which is accelerated by pure aluminum oxide, is appreciably retarded by the adsorption of sodium ions on the aluminosilicate. According to our results, pure aluminum oxide does not exchange-adsorb sodium ions from aqueous sodium acetate solutions and so cannot be poisoned for isomerization after treatment with this solution. The poisoning effect of the adsorption of sodium ions with respect to isomerization in presence of aluminosilicate indicates, in our opinion, that isomerizing power is possessed not only by the free aluminum oxide

existing in the catalyst, but also by those active aluminosilicate centers that promote cracking and hydrogen redistribution. This inference is in accord with the results that we have obtained for the dehydration of ethanol. For this reaction only aluminum oxide is active, and aluminosilicate does not alter in dehydration activity after treatment with aqueous sodium acetate. It is possible that isomerization at aluminosilicate active centers proceeds via the depolymerization of the isomerized polymer.

The results that we have obtained on polymerization do not resolve the question of whether this reaction proceeds at "acidic" centers, since, on the one hand, the dependence of activity on the composition of the catalyst is described for polymerization by a curve that is characteristic for catalysis at "acidic" aluminosilicate active centers, whereas, on the other hand, no appreciable poisoning of the catalyst with respect to polymerization was observed when 29 mg-equivalents of sodium per 100 g of catalyst was adsorbed. Further investigation of this reaction is now proceeding.

SUMMARY

1. A study has been made of the kinetics of the simultaneous reactions of polymerization, hydrogen redistribution, and isomerization under conditions precluding cracking, and it has been shown that the transformations of cyclohexene proceed at active centers of two types.

2. Hydrogen redistribution proceeds only at "acidic" aluminosilicate active centers. Isomerization proceeds at "acidic" active centers and on aluminum oxide.

3. Adsorption of sodium ions poisons aluminosilicate with respect to hydrogen redistribution and isomerization.

Received June 22, 1953

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CHEMICAL REACTIONS OF UNSATURATED AND MACROMOLECULAR COMPOUNDS

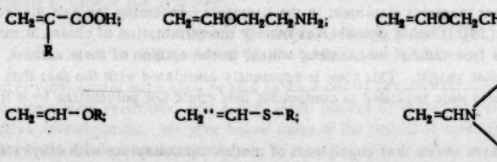
COMMUNICATION 2. COPOLYMERIZATION OF METHYL METHACRYLATE WITH ALKYL VINYL ETHERS

M. F. Shostakovsky and A. M. Khomutov

The development of investigations on polymerization and copolymerization has been characterized until recently by the utilization of the double bonds of various unsaturated compounds as the basis of the synthetic potentialities of these reactions.

New synthetic potentialities for polymerization and copolymerization reactions are now emerging as a result of the application in these reactions of new compounds having not only multiple bonds, but also active functional groups, i.e., other reaction centers that may be utilized in the processes that we are considering.

As examples of new compounds that we have applied in polymerization and copolymerization reactions, we will cite the following:

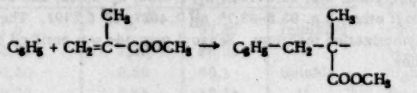


(R and R_1 may be Alk, Ar, aralkyl, or other radicals, which may contain substituents).

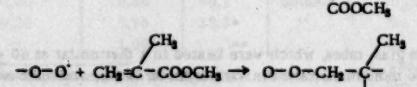
In our previous work [1] we have studied the behavior of methacrylic acid in copolymerization reactions with vinyl ethers. It was shown that, apart from the main copolymerization process, there were a number of simultaneous reactions associated with double bonds and functional groups containing mobile hydrogen. The presence in the molecules of several functional groups has a marked effect on the course of the polymerization of the original monomers, as compared, for example, with the polymerization of unsaturated compounds not containing active functional groups [2].

It was pointed out at the same time that alkyl vinyl ethers, which do not polymerize in presence of benzoyl peroxide [3] or oxygen [4], will copolymerize with methacrylic acid. It was of interest to establish the possibility of copolymerization between alkyl vinyl ethers and a methacrylic ester, in which the mobile hydrogen of the carboxyl group is absent.

In the literature there are only tentative statements concerning the possibility of copolymerization between methyl methacrylate and methyl vinyl ether [5]. From these results no information can be obtained concerning the ratio in which the original monomers will enter into copolymerization. In the present paper we give the results of a study of the copolymerization of methyl methacrylate with ethyl and butyl vinyl ethers, a wide range of monomer ratios being used. In this case, as in that of methacrylic acid, the copolymerization was smoothly effected in presence of benzoyl peroxide. Our explanation of this process is that methyl methacrylate contains the conjugated system $-C=C-C=O$, which is readily activated by oxygen [6] or by the free radicals formed by the decomposition of benzoyl peroxide [7], and that it initiates the chain according to Scheme 1 or 2, i.e., the function of benzoyl peroxide is more limited than it is considered to be by Gelissen and Hermans [8].



(1)



(2)

As our investigations have shown, compounds containing a conjugated system are suitable for copolymerization with alkyl vinyl ethers in presence of benzoyl peroxide. Hence, in the selection of components for copolymerization with alkyl vinyl ethers, we may take as one criterion the presence of conjugated double bonds in the original compound. The establishment, however, of a free-radical mechanism for the polymerization and copolymerization of vinyl ethers deserves close attention in its relation to the fact that the vinylation reactions of Favorsky and Shostakovsky [9] have opened up wide possibilities for the preparation of compounds containing both multiple bonds and various functional groups.

The present investigation has shown that increase in the concentration of the alkyl vinyl ether in the reaction mixture increases its content in the copolymer obtained. The structure of the latter may be represented as follows:

$$n\,CH_2{=}C(CH_3)COOCH_3 + m\,(CH_2{=}CHOC_2H_5) \rightarrow \cdots - \left[CH_2 - \underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}} - \right]_x - \left[-CH_2 - \underset{\displaystyle OC_2H_5}{CH} \right]_y - \cdots$$

The presence in the molecule of alkyl vinyl ether units affects the solubility, fusibility, and outward appearance of the copolymers. The results of the elementary analysis of these copolymers show that, according to the ratio of the original components, they may contain 6-21 mole-% of alkyl vinyl ether units.

The supposition that the original components may undergo separate polymerization was not confirmed, i.e., the reaction product was a copolymer, and did not contain methyl methacrylate polymers or alkyl vinyl ether polymers. There is a somewhat incorrect statement in the literature concerning the part played by vinyl ethers in copolymerization processes [10], it being described as merely the termination of chains formed by compounds that readily polymerize by the free-radical mechanism, which, in the opinion of these authors, leads to the formation of compounds of low molecular weight. This view is apparently associated with the fact that, before our investigations [11], alkyl vinyl ethers were regarded as compounds that could not polymerize by a free-radical mechanism [12-15].

Our investigations have shown that copolymers of methyl methacrylate with alkyl vinyl ethers have molecules that are similar in size to those of the corresponding polymers of the methyl methacrylate component. The relative degrees of polymerization and copolymerization of our products were estimated by comparison of the viscosities of solutions of these polymers and copolymers, and it was found that in some cases the viscosities of solutions of the copolymers were equal to, and in other cases higher than, the viscosities of solutions of methyl methacrylate polymers prepared under the same conditions (see Tables 2 and 4).

As shown in the experimental part of this paper (Tables 1 and 3), the yield of polymer falls as the concentration of methyl methacrylate falls and as that of the vinyl ether rises; at the same time qualitative changes occur owing to rise in the number of alkyl vinyl ether units (Tables 2 and 4). We may, therefore, suppose that methyl methacrylate carries the function of chain initiation. Elementary analysis indicates a greater content of methyl methacrylate units in the molecule, and this is confirmed by estimation of the monomers that have not entered the reactions. The balance sheet of the products of the polymerization reaction shows that methyl methacrylate, alkyl vinyl ether, and copolymer are present. The differences found in the physical properties of the polymer of methyl methacrylate and those of the copolymers confirm that copolymerization does indeed occur. These differences are concerned with solubility and fusibility, and they grow as the number of alkyl vinyl ether units present in the molecular chain increases.

Hence, it has been shown, on the basis of yields, elementary composition, solubility, and other physicochemical properties of the copolymers, that methyl methacrylate copolymerizes with alkyl vinyl ethers in presence of benzoyl peroxide.

EXPERIMENTAL

The starting materials were methyl methacrylate, b.p. 99.5-100°; n_D^{20} 1.4150; d_4^{20} 0.936; and ethyl vinyl ether, b.p. 35.9°; n_D^{20} 1.3778; d_4^{20} 0.7533; and butyl vinyl ether, b.p. 93.5-93.7°; n_D^{20} 1.4027; d_4^{20} 0.7791. The monomers were always freshly distilled for use in the polymerization reactions. Benzoyl peroxide was purified by two reprecipitations by methanol from chloroform solution.

Experimental Procedure

The copolymerization was carried out in glass tubes, which were heated in a thermostat at 60 ± 1°. The reaction mixture consisted of 25 g altogether of the monomers, taken in various molar ratios, and 0.2% on the total weight of monomers of benzoyl peroxide. The process proceeded continuously until solid or highly viscous products were

obtained. At the end of the process the tubes were cooled to 0°. Control experiments were carried out under the same conditions on the polymerization in presence of benzoyl peroxide of the pure monomers: methyl methacrylate, and ethyl and butyl vinyl ethers. The purification and treatment of the reaction products were carried out as follows: they were dissolved in acetone and precipitated by methanol, dissolution and precipitation being repeated until there was a negative reaction for acetaldehyde with Schiff's reagent; the polymers and copolymers were then dried to constant weight.

The selective solubilities of the polymers and copolymers obtained were then determined. After treatment with selective solvents, the polymers and copolymers were precipitated with methanol, dried to constant weight, and analyzed for C and H. On the basis of the results, the compositions of the copolymers were calculated. Also, their fusibilities and viscosities were determined [16].

In all tests on the copolymers, a control sample of polymethyl methacrylate was taken for comparison. In order to check the ability of the monomers used to undergo free-radical polymerization, the following control tests were made.

1. A study of the tendency of methyl methacrylate to undergo polymerization in presence of benzoyl peroxide was carried out by the above-described procedure, the duration of the reaction being 40 hours. This polymer was soluble in acetone, and appreciably less soluble in benzene and dioxane. The polymer partly dissolved in boiling ethanol, and it dissolved completely in a boiling mixture of butyl alcohol and butyl vinyl ether; when the solutions were cooled it was reprecipitated. It was insoluble in alkyl vinyl ethers. The purified polymer was found to contain the following amounts of carbon and hydrogen:

Found %: C 60.24; 60.28; H 8.30; 8.28
Calculated %: C 59.99; H 8.00

2. Ethyl and butyl vinyl ethers were each heated in presence of benzoyl peroxide for 40 hours. After fractionation, the original ethers were recovered, and a very small residue of resinified material remained; it was insufficient for quantitative investigations. We give below some of the results of investigations on the copolymerization of alkyl vinyl ethers with methyl methacrylate.

Copolymerization of Methyl Methacrylate with Ethyl Vinyl Ether

The amounts taken for the copolymerization were 7.9 g of methyl methacrylate and 17.1 g of ethyl vinyl ether (i.e., a molar ratio of 1:3). The duration of heating was 40 hours. The contents of the tube became highly viscous. The conditions for the copolymerization and the purification are described above. It was found that the copolymer was soluble in a hot 85:15 mixture of ethanol and dioxane, and the solution remained clear when cold. At a similar concentration polymethyl methacrylate did not dissolve completely in the hot solvent, and when the solution was cooled it was reprecipitated. The copolymer was dissolved in the mixture of ethanol and dioxane, precipitated from solution with methanol, dried to constant weight, and subjected to microanalysis.

The above-described procedure for the copolymerization of methyl methacrylate with ethyl vinyl ether was carried out also at other monomer ratios. The monomer ratios and yields are given in Table 1, in which the solubilities of the copolymers in the mixture of ethanol and dioxane are also given. The microanalytical results on the copolymers are given in Table 2.

TABLE 1

Monomer Ratios and Yields of Copolymers

No.	Molar ratios		Yield of polymer or copolymer (%)	Solubility in 15:85% dioxane/ethanol
	$CH_2=C(CH_3)COOCH_3$	$CH_2=CHOC_2H_5$		
1	1.0	—	97.32	Insoluble
2	0.75	0.25	86.30	"
3	0.50	0.50	60.1	Soluble
4	0.25	0.75	33.5*	"
5	—	1.00	**	

* Apart from copolymer, 60% of ethyl vinyl ether and 51% of methyl methacrylate were isolated.
** 96.3% of ethyl vinyl ether was isolated.

When the copolymers were heated in crucibles, some of them melted, forming vitreous masses. This behavior was particularly characteristic for copolymers containing a high proportion of alkyl vinyl ether units.

Copolymerization of Methyl Methacrylate with Butyl Vinyl Ether

The amounts taken for the copolymerization were 6.25 g of methyl methacrylate and 18.75 g of butyl vinyl ether (i.e., a molar ratio of 1:3). The duration of heating was 40 hours. The contents of the tube became highly viscous. The copolymerization conditions and the method of purification of the copolymer are described above. The copolymer did not dissolve completely when heated with a mixture of ethanol and dioxane, but was readily soluble in a 1:1 mixture of butyl alcohol and butyl vinyl ether; polymethyl methacrylate was

TABLE 2

Compositions of Copolymers

No.	Molar ratios		Amount of		Mol. proportions of units in copolymer (%)		Viscosity	
	$CH_2=C(CH_3)COOCH_3$	$CH_2=CHOC_2H_5$	C (%)	H (%)	$CH_2-C(CH_3)COOCH_3$	$-CH_2-CH(OC_2H_5)-$	η_{sp}/c (stokes/sec)	η_{rel}
1	1.0	–	60.24	8.30	–	–	0.011	1.5011
			60.28	8.28				
2	0.75	0.25	60.22	8.35	93.45	6.55	0.041	5.4992
			60.43	8.44				
3	0.5	0.5	60.61	8.17	85.35	14.65	0.0268	3.5819
			60.85	8.36				
4	0.25	0.75	61.13	8.33	78.35	21.65	0.013	1.8001
			61.05	8.46				
5	–	1.0	–	–	–	–	–	–

found to be insoluble in the latter solvent. In this, as in the previous, series of experiments, no polymer of methyl methacrylate was isolated. The copolymer was precipitated from solution with methanol and dried to constant weight. The carbon and hydrogen contents were then determined by microanalytical methods.

The copolymerization of methyl methacrylate with butyl vinyl ether was carried out also at other monomer ratios. The yields of copolymers are given in Table 3.

TABLE 3

Monomer Ratios and Yields of Copolymers

No.	Molar ratios		Yield of polymer or co-polymer (%)	Solubility in 50:50 butyl alcohol/butyl vinyl ether
	$CH_2=C(CH_3)COOCH_3$	$CH_2=CHOC_4H_9$		
1	1.0	–	97.32	Insoluble
2	0.75	0.25	76.5	Soluble
3	0.50	0.50	60.7	"
4	0.25	0.75	27.0	"
5	–	1.0	*	

* Unchanged butyl vinyl ether was recovered.

After being dried, the copolymers were subjected to selective dissolution in a mixture of butyl alcohol and butyl vinyl ether, and were then precipitated with methanol, dried to constant weight in a vacuum drier at 30-35° (4 mm), and sent for microanalysis. The microanalytical results and the calculated compositions of copolymers are given in Table 4, in which their viscosities are also given. When heated, the copolymers melted, forming vitreous masses.

SUMMARY

1. A study has been made of the copolymerization of methyl methacrylate with alkyl vinyl ethers in presence of benzoyl peroxide at various monomer ratios.

TABLE 4

Compositions of Copolymers

No.	Molar ratios		Amount of		Mol. proportions of units in copolymer (%)		Viscosity	
	$CH_2=O(CH_3)COOCH_3$	$CH_2=CHOC_4H_9$	C (%)	H(%)	$CH_2-C(CH_3)(-)COOCH_3$	$-CH_2-CHOC_4H_9$	η_{sp}/c (stokes/sec)	η_{rel}
1	1.00	–	60.24	8.30	100	–	0.011	1.5016
			60.28	8.28				
2	0.75	0.25	61.93	8.47	86.4	13.6	0.015	2.0299
			61.73	8.32				
3	0.50	0.50	61.65	8.67	86.4	13.6	0.016	2.1719
			61.61	8.47				
4	0.25	0.75	62.68	8.92	76.33	23.67	0.0126	1.6932
			62.99	9.02				
5	–	1.00	–	–	–	–	–	–

2. Copolymers of methyl methacrylate with alkyl vinyl ethers have been prepared.

3. It has been shown that, in presence of benzoyl peroxide, copolymerization may be effected between alkyl vinyl ethers and compounds containing the system of double bonds: $-C=C-C=O$.

4. In the copolymerization of methyl methacrylate with alkyl vinyl ethers in presence of benzoyl peroxide, no polymers of methyl methacrylate were detected.

Received March 20, 1953

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CHEMICAL METHOD OF INVESTIGATING THE METAL–HYDROGEN NATURE OF A SKELETAL NICKEL CATALYST

L. Kh. Freidlin and K. G. Rudneva

By analogy to the promoting effect of gases on metal films [1], it may be supposed that hydrogen plays a determining role in the activity of a skeletal (Raney) catalyst. It is known that such catalysts contain considerable amounts of hydrogen, attaining several hundredths of a milliliter per gram of nickel. It was necessary to work out a method that would make it possible to establish a relationship between the activity of a skeletal catalyst and the presence of hydrogen in the catalyst. The physical method of removing hydrogen by prolonged continuous pumping at high temperature has the serious defect that under these conditions the structure of the catalyst may be changed, so that it may be almost impossible to separate the effect of hydrogen removal on the properties of the catalyst from the effect of the thermal treatment. Unlike the physical method, the chemical method enables the hydrogen removal to be carried out at close to room temperature, at which the physical structure of the catalyst does not alter, and it is permissible, therefore, to study the changes in the properties of a skeletal catalyst from which hydrogen has been removed chemically by means of substances that can be hydrogenated.

The correct selection of substances suitable for this purpose is extremely important. The hydrogen-removing agent must rapidly and completely extract the hydrogen present in the nickel. The reagent and its hydrogenation products must not react with the metal or block its active surface, and they must be readily analyzed. After the process, the catalyst must be quantitatively separated from the hydrogenatable substance by filtration, and must be analyzed. If the hydrogenatable substance is volatile, then it is difficult to avoid losses, and the agent must, therefore, have a high boiling point. The previously used hydrogen-removing agents —butyl vinyl ether, nitrobenzene, and cyclopentene [2]— were readily volatile, not readily accessible, or difficult to analyze. We have succeeded in finding a hydrogen-removing agent that does not suffer from these defects, and in establishing the optimum conditions for the removal of hydrogen from the catalyst.

The chemical method for the removal of hydrogen serves at the same time as a method for the determination of the amount of chemically active hydrogen in the catalyst. The results of duplicate tests on the hydrogen content of the catalyst generally agree within 1-2%. By means of the chemical method of hydrogen removal we have established the nonequivalence of the two forms of hydrogen contained in the catalyst and the existence of a relationship between the activity of a catalyst and its hydrogen content [2]. Sokolsky and co-workers [3] have reached the same conclusion by the use of an independent potentiometric method. On the basis of results obtained by the chemical method we predicted the possibility of restoring the activity of an inert catalyst by treatment with hydrogen, and we have confirmed this experimentally [4].

We have recently shown that the activity of a skeletal nickel catalyst that has been partly "dehydrogenated" and deactivated by treatment at 300° in a vacuum in absence of organic hydrogen-removing agents can also be restored by treatment with hydrogen. The results obtained by the physical method are, therefore, similar to those obtained by the method of chemical removal of hydrogen. Aubry [5] has suggested that the reducing action of skeletal nickel in aqueous medium on sulfites, thiosulfates, selenites, and other compounds at room temperatures is to be explained by its ability to react with evolution of hydrogen:

$$Ni + 2H_2O = Ni(OH)_2 + H_2.$$

The film of nickel hydroxide protects the metal and preserves its activity.

We have established by special experiments that, after treatment with water vapor for two hours at temperatures of up to 200°, the catalyst fully retains its activity. Hence, even at this high temperature a skeletal nickel catalyst does not react with water vapor and does not become covered with a film of hydroxide that will block its active surface. We have shown also that the amount of determinable hydrogen in the nickel does not depend on whether the benzoquinone with which it has been treated was dissolved in moist dioxane or in dioxane that had been twice distilled over sodium.

Conditions for the Removal of Hydrogen from the Catalyst by means of Benzoquinone

It was found that benzoquinone most satisfactorily fulfils the requirements for a hydrogen-removing agent for use in the chemical method. It is convenient to treat the catalyst with benzoquinone in dioxane, in which the intermediate and final reaction products, quinhydrone and hydroquinone, are also readily soluble. The dioxane was freshly distilled, and did not contain peroxy compounds. The reaction was carried out in a hydrogenation flask attached to a powerful shaker and connected to a gas buret. The flask was provided with a jacket for heating, and with two tubes for the introduction of catalyst and hydrogenatable substance and for the entry and exit of gases. A No. 3 glass filter was fused into one of the outlet tubes. The flask was heated with water taken from an ultrathermostat and circulated through the jacket. A spoonful of the catalyst paste, leveled by means of a glass rod, was taken for each experiment, so that practically equal weights of catalyst were taken on each occasion.

Removal of hydrogen from the catalyst was carried out as follows: Air was displaced from the flask with hydrogen, and, in a current of hydrogen, the catalyst was washed through a funnel into the flask with the aid of 5-10 ml of solvent. The outlet tube was closed with a ground stopper, the shaker was switched on, and the catalyst was saturated with hydrogen. When the absorption of hydrogen ceased or did not exceed 0.1 ml per minute, saturation of the catalyst was regarded as complete. Hydrogen was carefully displaced from the flask with nitrogen, and, in a current of nitrogen, a definite volume of a 3% solution of benzoquinone in dioxane was introduced. The motor was switched on, and shaking began. Under these conditions benzoquinone could be hydrogenated to hydroquinone, but only by hydrogen contained in the catalyst. Hydrogenation to cyclohexanediol would require a much higher temperature.

After treatment of the catalyst with benzoquinone in an atmosphere of nitrogen, the catalyst was filtered off and washed 5-6 times with dioxane to effect complete removal of benzoquinone and its hydrogenation products. The completeness of the removal of benzoquinone was checked by the reaction with iodine in an alkaline medium [6]. The washings were united with the main filtrate, and the contents of hydroquinone and of residual benzoquinone were determined iodometrically [7, 8]. From the results of this analysis, the amount of hydrogen extracted from the catalyst by benzoquinone was calculated. The activity of the catalyst was then determined.

The removal of hydrogen from the catalyst by means of benzoquinone in absence of an external hydrogen source led to breakdown of its active structure and to deactivation. At 20°, fairly complete deactivation of the catalyst was attained only after treatment for 120 minutes with benzoquinone (an excess with respect to the hydrogen in the catalyst). When the temperature was raised to 60°, the time required for the deactivation of the catalyst was reduced to 60 minutes. The catalyst, removed from the liquid and washed carefully, would not absorb hydrogen and was completely inactive for the hydrogenation of organic compounds at 20°.

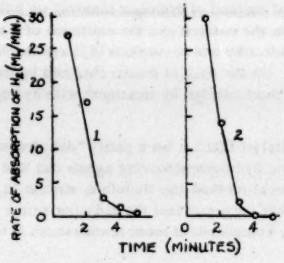

Fig. 1. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in two successive experiments (1 and 2) in alcohol at 20° with 1 g of skeletal nickel catalyst.

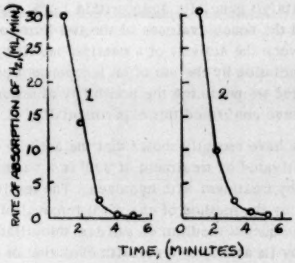

Fig. 2. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° with 1 g of skeletal nickel catalyst: 1) freshly prepared; 2) after keeping for 6 months under water.

Method of Testing the Activity of the Catalyst

The activity of the catalyst was determined from the rate of hydrogenation of phenyl vinyl ether in ethanol at 20° under normal pressure. The phenyl vinyl ether had b.p. 155-156° and n_D^{20} 1.5225. This substance does not remove hydrogen from the catalyst in the process of hydrogenation, it is of low volatility, and it is readily analyzed iodometrically. It was established by special experiments that the activity of a given portion of catalyst does not fall in a series of successive hydrogenations of phenyl vinyl ether (Fig. 1).

The samples of catalyst were prepared by a two-hour leaching of a 50% Ni–Al alloy with 20% caustic soda at 100-105°. In one of these, in the freshly prepared form, 176 ml of hydrogen was found per gram of catalyst. After being kept for six months under water, it was found to contain 173 ml of hydrogen per gram, and its activity had not changed (Fig. 2).

Fig. 3 shows the rate curves for the hydrogenation of phenyl vinyl ether at 20° in presence of various amounts of catalyst: 0.25, 1, and 2 g. It will be seen from Fig. 3 that, when the amount of catalyst is increased from 1 g to 2 g, the rate of the reaction remains practically unchanged. On the other hand, when the amount of catalyst is reduced to 0.25 g, not only the reaction rate, but also the character of the kinetics changes. The apparent zero-order reaction that is found when there is insufficient catalyst in the system may be explained by the hypothesis that the reaction rate is limited in this case by the rate at which hydrogen is activated on the catalyst. In our experiments, 1 g of catalyst was used.

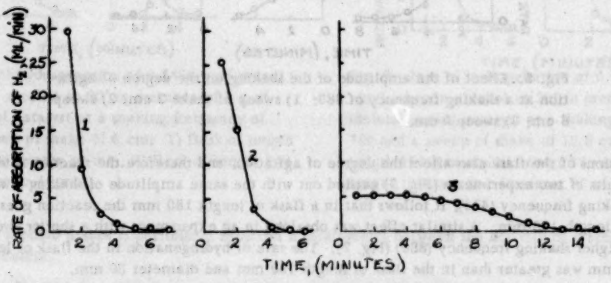

Fig. 3. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether at 20° in alcohol: 1) with 2 g of skeletal nickel catalyst; 2) with 1 g; 3) with 0.25 g.

Effect of the Amplitude of Shaking and the Dimensions of the Flask on the Degree of Agitation and the Rate of Hydrogenation

In order to exclude the effect of the rate of diffusion of the reacting components to the catalyst surface when studying the kinetics of the reaction, we carried out a series of experiments with the object of determining the effect of the amplitude of shaking and the dimensions of the flask on the degree of agitation. A study was made of the rate of hydrogenation of 0.2495 g of phenyl vinyl ether in 15 ml of alcohol in presence of 1 g of catalyst. At first experiments were carried out in a flask of smaller dimensions: length 150 mm and internal diameter 30 mm. It will be seen from the curves in Fig. 4 that with a shaking frequency of 470 complete oscillations the reaction rate is considerably higher when the sweep of the shake is 9 cm than when it is 3 cm. An analogous increase in reaction rate is observed when the frequency of shaking is increased. Comparing the results of three experiments carried out at 880

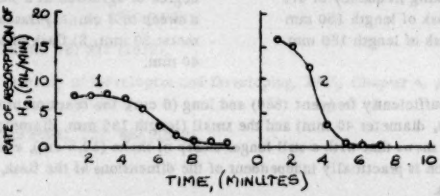

Fig. 4. Effect of the amplitude of the shaking on the degree of agitation at a shaking frequency of 470: 1) total sweep of shake 3 cm; 2) total sweep 9 cm.

oscillations per minute (Fig. 5), we see that in the experiment with the shortest sweep (3 cm) the reaction is slower than in the experiment with a longer sweep (6 cm). Further increase in the sweep of the shake (9 cm) did not increase the reaction rate.

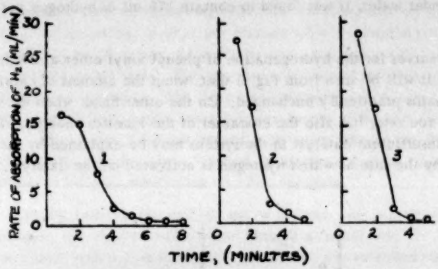

Fig. 5. Effect of the amplitude of the shaking on the degree of agitation at a shaking frequency of 880: 1) sweep of shake 3 cm; 2) sweep 6 cm; 3) sweep 9 cm.

The dimensions of the flask also affect the degree of agitation, and therefore the reaction rate. From a comparison of the results of two experiments (Fig. 6) carried out with the same amplitude of shaking (sweep of 9 cm) and with the same shaking frequency (470), it follows that in a flask of length 180 mm the reaction goes more rapidly than in a flask of length 150 mm. A similar effect was obtained in an experiment with a shorter sweep of shake (3 cm), but with a higher shaking frequency (880) (Fig. 7). The rate of hydrogenation in the flask of length 240 mm and diameter 40 mm was greater than in the flask of length 150 mm and diameter 30 mm.

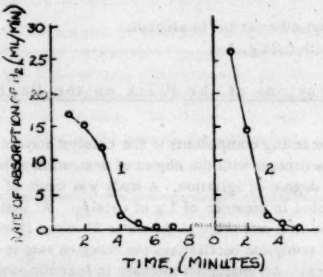

Fig. 6. Effect of the dimensions of the flask on the degree of agitation at a shaking frequency of 470 and a sweep of 9 cm: 1) flask of length 150 mm and diameter 30 mm; 2) flask of length 180 mm and diameter 30 mm.

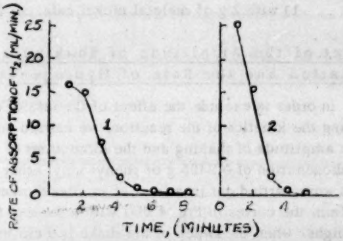

Fig. 7. Effect of the dimensions of the flask on the degree of agitation at a shaking frequency of 880 and a sweep of 3 cm: 1) flask of length 150 mm and diameter 30 mm; 2) flask of length 240 mm and diameter 40 mm.

When the shakes are sufficiently frequent (880) and long (6 cm), the reaction proceeds at the same rate in the large (length 240 mm, diameter 40 mm) and the small (length 150 mm, diameter 30 mm) flasks, as will be seen from Fig. 8. Fig. 9 shows that with a still longer sweep of shake (10.5 cm), even at a lower frequency (700), the rate of the reaction is practically independent of the dimensions of the flask, being identical in the small and in the large flasks.

Thus, sufficiently vigorous agitation in the system can be ensured not only by increase in the rate of shaking, but also by changes in the amplitude of the shake and in the dimensions of the reaction vessel.

SUMMARY

1. A chemical method for the removal of hydrogen from a skeletal nickel catalyst is described; it serves at the same time as a method for the determination of the amount of chemically active hydrogen contained in the metal.

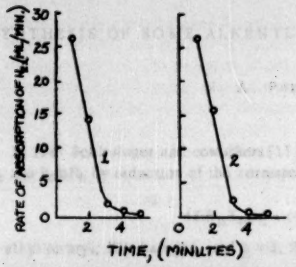

Fig. 8. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of skeletal nickel catalyst at a shaking frequency of 880 and a sweep of shake of 6 cm: 1) flask of length 150 mm and diameter 30 mm; 2) flask of length 240 mm and diameter 40 mm.

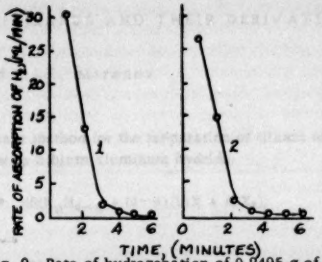

Fig. 9. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of skeletal nickel catalyst at a shaking frequency of 700 and a sweep of shake of 10.5 cm: 1) flask of length 150 mm and diameter 30 mm; 2) flask of length 180 mm and diameter 30 mm.

2. The method makes it possible to establish a relationship between the activity of a skeletal catalyst and its hydrogen content.

3. The effect of the amount of catalyst, the amplitude of the shake, and the dimensions of the flask on the reaction rate is also investigated.

Received April 29, 1953

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SYNTHESIS OF SOME ALKENYL- AND ALKYL-SILANES AND THEIR DERIVATIVES

V. A. Ponomarenko and V. F. Mironov

In 1947 Schlesinger and coworkers [1] proposed a convenient method for the preparation of silanes of the type $RSiH_3$ and R_2SiH_2 by reduction of the corresponding halosilanes with lithium aluminum hydride:

$$4SiR_nX_{4-n} + (4-n)LiAlH_4 \xrightarrow{\text{ether}} 4SiR_nH_{4-n} + (4-n)(LiX + AlX_3), \qquad (1)$$

(R is alkyl or aryl, X is halogen, and n = 1, 2, or 3).

The discoverers of the method, and also other investigators [2], have noted that in certain cases lithium hydride can be used for this purpose, but the resulting yield of alkylsilanes was then lower, and it was found that an elevated temperature and a three- or four- fold excess of lithium hydride were necessary.

In this series of silanes, compounds containing unsaturated radicals, or radicals containing halogen, are unknown. It might be thought that both $LiAlH_4$ and LiH could be used for their synthesis. When, however, $LiAlH_4$ is used, it is quite possible that the products will undergo polymerization or isomerization under the influence of the considerable amounts of AlX_3 formed in the reaction of Equation 1. Allyltrimethylsilane, for example, polymerizes vigorously in presence of $AlCl_3$ under mild conditions [3], and (chloromethyl)trimethylsilane readily undergoes rearrangement to chloroethyldimethylsilane [4]. Hence, in order to avoid these undesirable reactions, all reductions were effected with lithium hydride, which, moreoever, is considerably more readily accessible than $LiAlH_4$. The expediency of making extensive application of lithium hydride has recently been pointed out by one of us and Petrov [5] with respect to the synthesis of the silicon analogs of propane, butane, pentane, and cyclohexane.

Continuing this line of investigation, we have found that $(C_2H_5)_2Si(OC_2H_5)_2$ is reduced by lithium hydride to $(C_2H_5)_2SiH_2$. This first indication of the possibility of the replacement of an ethoxyl group attached to silicon by hydrogen is important also because $LiAlH_4$, which cannot form the harmful AlX_3 with alkoxysilanes, may be used if desired. The reduction of allyltrichlorosilane with lithium hydride resulted in a relatively low yield (37%) of allylsilane. Diallylsilane was obtained similarly in 37% yield. The compounds obtained are quite stable liquids having an odor that is characteristic for the whole series of allylsilanes [6]. Diallylsilane combines quantitatively at the double bonds with thiocyanogen, without any side reactions.* This fact is of importance in that the quantitative determination of the unsaturation of allylsilanes by the bromine-number method gives indefinite results, since bromine causes β-decomposition and reacts with the Si—H bond.

Allylsilane slowly combines with hydrogen chloride. An attempt to distill the chloro compound so formed resulted in its decomposition at about 80°.**

$$H_3SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCl \rightarrow H_3SiCl + CH_2{=}CHCH_3. \qquad (2)$$

In a vacuum (2-chloropropyl)silane can be distilled without decomposition. When it is treated with Grignard reagents —allylmagnesium bromide and ethylmagnesium bromide— reaction occurs. However, although no signs of β-decomposition are noted in the case of allylmagnesium bromide (absence of gas evolution), with ethylmagnesium bromide β-decomposition occurs, as is shown by the vigorous evolution of gas:

$$H_3SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCl + C_2H_5MgBr \rightarrow H_3SiC_2H_5 + CH_2{=}CHCH_3 + MgClBr. \qquad (3)$$

In neither case was it found possible to isolate any individual condensation products, formed in accordance with the scheme for the reaction of β-halo compounds with RMgX that we have investigated previously [6, 8, 9], although a considerable amount of high-boiling (100-160°) products was formed. The thermal instability and β-decomposition

* The addition of thiocyanogen was kindly carried out by A. A. Bugorkovskaya, who has developed the method and has determined thiocyanogen numbers for more than 25 alkenylsilanes.

** It is very probable that this reaction will provide a convenient method for the preparation of difficultly accessible [7] halosilanes of the type H_3SiX.

of this chloro compound under the influence of Grignard reagents proves that it is a β-chloro compound, i.e., that HCl adds to allylsilane (as also to other allylsilanes [3, 6, 8, 9, 10]) according to Markovnikov's rule.

As we now had a β-chloro compound of the structure indicated, it was of interest to prepare an α-chloro compound for comparison of properties. With this object, Cl_3SiCH_2Cl was reduced with lithium hydride. The course of the reaction was such that only chlorine attached to silicon was replaced by hydrogen, the chlorine attached to carbon being left untouched. The resulting α-chloro compound, unlike the β compound, was a stable liquid that did not decompose when distilled or stored. Both chloro compounds were of pleasant odor, thus indicating absence of chlorine attached to silicon. Among the physical properties of the sila-hydrocarbons obtained, the melting points and molecular refractions are of interest.

It is clear from the work of Petrov and Chernyshev [11] that the melting points of tetra-substituted silanes are lower than those of the structurally similar tetraalkylmethanes. It was of interest to determine the melting points of straight-chain silanes and to determine the effect of the presence of double bonds and of the position of the silicon atom in the chain. For this purpose, and also in order to make a comparison of other physical properties, hexylsilane and dipropylsilane were synthesized by the above-described method [5]. The melting points of diallylsilane, dipropylsilane, and hexylsilane are given, together with that of heptane for comparison, in Table 1.*

TABLE 1

Substance	Formula	M.p. (°C)
Diallylsilane	$CH_2=CHCH_2SiH_2CH_2CH=CH_2$	−115
Dipropylsilane	$CH_3CH_2CH_2SiH_2CH_2CH_2CH_3$	−113
Hexylsilane	$CH_3CH_2CH_2CH_2CH_2CH_2SiH_3$	− 98
Heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	− 90.6

It will be seen from Table 1 that the introduction of double bonds into the hydrocarbon chains of silanes (for example, passing from dipropyl- to diallylsilane) has practically no effect on the melting point. On the other hand, the movement of the silicon atom from the periphery (hexylsilane) to the center (dipropylsilane) results in a considerable lowering of the melting point. Also, these silicon analogs of heptane melt lower than heptane itself.

Comparison of the calculated [12] and found values of the molecular refraction for mono- and di-allylsilanes reveals a quite definite discrepancy, such as was observed previously for a number of substituted allylsilanes [6, 8, 9]. This discrepancy is to be explained by the fact that the value assumed in the literature [12] for the refraction of the Si−C bond is 2.50 ml/mole for all alkyls, although this value is satisfactory only for methyl. On the basis of experimental data for a large number of allyl-substituted silanes, we have found the refraction of the Si−C bond (when C belongs to allyl) to be 2.68 ml/mole.

Analysis of the data for a series of alkyltriethylsilanes [13] shows that, for the ethyl radical also, the value for the Si−C bond differs somewhat from the value given above and should evidently be taken to be 2.38 ml/mole. If we take these corrections into consideration, then, as Table 2 shows, for the majority of sila-hydrocarbons containing ethyl and allyl radicals, the discrepancy between calculated and found refractions almost disappears.

TABLE 2

Formula of compound	MR					Literature reference
	found	calculated [12]	Δ	calcd. by us	Δ	
$(C_2H_5)_4Si$	48.34	48.8	−0.46	48.32	+0.02	[13]
$(C_2H_5)_2SiH_2$	30.63	30.80	−0.17	30.56	+0.07	This investigation
$(C_2H_5)_3SiC_3H_5$	52.72	52.96	−0.24	52.78	−0.06	[8]
$C_6H_5(CH_3)_2SiC_3H_5$	59.07	58.89	+0.18	59.07	0.00	[6]
$(CH_3)_2SiC_3H_5$	39.20	39.07	+0.13	39.25	−0.05	[3]
$H_3SiC_3H_5$	26.15	25.96	+0.19	26.14	+0.01	This investigation
$(CH_3)_2Si(C_3H_5)_2$	48.20	47.86	+0.34	48.22	−0.02	[9]
$H_2Si(C_3H_5)_2$	39.48	39.12	+0.36	39.48	0.00	This investigation
$CH_3Si(C_3H_5)_3$	57.20	56.65	+0.55	57.19	+0.01	[9]
$C_6H_5Si(C_3H_5)_3$	76.90	76.47	+0.43	77.01	−0.11	[6]
$Si(C_3H_5)_4$	66.16	65.44	+0.72	66.16	0.00	[14]

* The melting point determinations were carried out by V. A. Volnova by the method of solidification and melting curves. We take the opportunity of expressing our sincere thanks to her.

EXPERIMENTAL

Lithium Hydride

Lithium hydride was prepared from lithium and hydrogen at 690-700° in an apparatus having an output of about 150 g lithium hydride per day. In principle, this apparatus was similar to that already described by Albert and Mahé [15], but differed from it in being simpler to construct and use. The differences were essentially as follows: a) gas heating was replaced by electric, and the reaction temperature was maintained constant within ± 10° by means of an electronically operated regulator; b) the reactor was appreciably simplified, water-cooling of the flanges being dispensed with, the protective jacket removed, rubber packing replaced by copper, and the bolts of the reactor head made hollow to enable them to be water-cooled; c) one beaker, instead of two, was used in the reactor; d) so that the reactor could be cooled more rapidly at the end of the experiment, the electric furnace was made of two insulated halves joined together by hinges so that it could be opened out for removal.

The yield of LiH was quantitative; about 1 kg was prepared. It was carefully ground in a steel ball mill filled with steel balls. At first it was passed through a sieve having 200 mesh per inch, but it was later found that it could be used successfully in the reaction without being sieved, since the milling in the ball mill rendered it sufficiently fine.

Dibutyl and Diisopentyl Ethers

The ethers were prepared in the usual way from the alcohols, dried over $CaCl_2$ and over sodium, and distilled over a small amount of LiH through a 20-plate column.

Allyltrichlorosilane $CH_2=CHCH_2SiCl_3$

Allyltrichlorosilane was synthesized in two ways.

1. Direct synthesis [16]. Allyl chloride, diluted with nitrogen, was passed over silicon-copper alloy at 290-300°. The reaction tube rapidly became clogged with polymerization products. From 800 g of the crude mixture, 35 g of allyldichlorosilane, b.p. 96.0-98.0°, and 48 g of allyltrichlorosilane, b.p. 115.5-117.0°, were isolated. In addition $HSiCl_3$, C_3H_5Cl, $SiCl_4$, and higher-boiling products were always isolated.

2. Organomagnesium synthesis. A few milliliters of allyl bromide were added to 97 g (4 moles) of magnesium in 1500 ml of ether in a two-liter flask. When the reaction had started, the contents of the flask were stirred for 11 hours while addition was made (at about 100 drops per minute) of a mixture of 500 g (3 moles) of $SiCl_4$ and 242 g (2 moles) of allyl bromide. The contents of the flask were boiled for four hours, filtered, and fractionated, yielding 130 g (37.4%) of allyltrichlorosilane, b.p. 116-118° (737 mm); n_D^{18} 1.4455; In addition, 20 g of diallylchlorosilane, b.p. 165-170°, was obtained.

This method is considerably more convenient than the direct synthesis [16] and the synthesis requiring the preliminary preparation of allylmagnesium bromide [17].

Allylsilane $CH_2=CHCH_2SiH_3$

A mixture of 110 g of allyltrichlorosilane, 45 g of lithium hydride, and 150 ml of diisopentyl ether was prepared in a still incorporating a small fractionating column. Allylsilane was distilled over periodically and collected in a trap. After the reaction mixture had been boiled for two days, 16.5 g (37%) of allylsilane, b.p. 17.0-20.0° had collected. After fractionation through a 35-plate column the allylsilane had the following constants: b.p. 18.9° (736.3 mm); d_4^4 0.6764; n_D^4 1.4050; found MR 26.15; calculated MR 26.14.

Diallylsilane $(CH_2=CHCH_2)_2SiH_2$

Under similar conditions, 33 g of diallyldichlorosilane and 10 g of lithium hydride in 50 ml of diisopentyl ether yielded 7.5 g of diallylsilane, which, after two fractionations through a 35-plate column, had the following constants: b.p. 103.7° (740.3 mm); d_4^{20} 0.7533; n_D^{18} 1.4420; found MR 39.48; calculated MR 39.48.

	Found %	C 63.78; 63.86;	H 10.67; Si 25.36; 25.17
$C_6H_{12}Si$.	Calculated %:	C 64.21;	H 10.78; Si 25.01

Yield of diallylsilane: 37%.

(2-Chloropropyl)silane $H_3SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCl$

Hydrogen chloride was passed through 15 g (0.2 mole) of allylsilane contained in a Drechsel bottle and cooled to −79°, until the weight increased by 10 g. The Drechsel bottle was then left in a freezing mixture in a Dewar

vessel overnight. The reaction product, after removal of HCl under vacuum, was found to be practically pure (2-chloropropyl)silane (n_D^{20} 1.4305), the yield being 18 g. When vacuum-distilled it gave no other fractions and had the following constants: b.p. 30.5° (140 mm); n_D^{20} 1.4305; d_4^{20} 0.8983; found MR 31.27; calculated MR 31.27.

Dipropylsilane $(C_3H_7)_2SiH_2$

A mixture of 35 g of dichlorodipropylsilane (b.p. 173-175°; prepared from $SiCl_4$ and C_3H_7MgBr), 15 g of lithium hydride, and 45 ml of dry diisopentyl ether was prepared in a still incorporating a small fractionating column. The reaction mixture was boiled, and the reaction product was distilled over periodically. A mixture (20 ml) of dipropylsilane and diisopentyl ether was collected, and this was fractionated over lithium hydride at 758 mm through a 20-plate column. Yield of dipropylsilane: 37% (from fractionation curve). The following fractions were obtained:

Fraction I, b.p. 32-110.4°; 2.4 ml; n_D^{20} 1.4009;

Fraction II, b.p. 110.4-111.0°; 5.9 ml; n_D^{20} 1.4110; d_4^{20} 0.7183

Fraction III, b.p. 110-149.0°; 1.8 ml; n_D^{20} 1.4105

Found: MR 40.18
Calculated: MR 40.06

These constants are in good agreement with data in the literature: b.p. 111°; d_4^{20} 0.7194; n_D^{20} 1.4112 [1].

Found %: C 62.03; 61.91; H 14.19; 14.03; Si 24.44; 24.14
$C_6H_{16}Si$. Calculated %: C 61.99; H 13.87; Si 24.14

Hexylsilane $C_6H_{13}SiH_3$

The trichlorohexylsilane $C_6H_{13}SiCl_3$ required for the reduction was prepared in two ways: a) from $C_6H_{13}MgBr$ and $SiCl_4$, 378 g (64%) of b.p. 189-192° being obtained (the literature [3] gives b.p. 127° (98 mm)); and b) from 1-hexene (b.p. 62.5-64°) and trichlorosilane (b.p. 31-32°) in presence of benzoyl peroxide. In one of these experiments, 4.2 g of 1-hexene, 15 g of $HSiCl_3$, and 0.9 g of freshly recrystallized benzoyl peroxide were taken. The reaction was carried out at 100° in a glass test tube contained in a 50-ml autoclave; it was continued for several days. The product was 7 g of trichlorohexylsilane, b.p. 188-191°; yield 64% on 1-hexene taken.

For the preparation of hexylsilane, 35 g of trichlorohexylsilane, 17 g of LiH, and 50 ml of diisopentyl ether were taken. A mixture (20 ml) of hexylsilane and diisopentyl ether was collected. Fractionation through a 20-plate column at 751 mm yielded the following fractions:

Fraction I, b.p. 111.5-114.0°; 2.2 mg; n_D^{20} 1.4109

Fraction II, b.p. 114.0-114.5°; 10.0 mg; n_D^{20} 1.4129; d_4^{20} 0.7182

Fraction III, b.p. 114.5-148.0°; 4.2 mg; n_D^{20} 1.4122

Found: MR 40.35
Calculated: MR 40.32

Found %: C 62.00; 61.74; H 14.00; 13.70; Si 24.05; 24.32
$C_6H_{16}Si$. Calculated %: C 61.99; H 13.87; Si 24.14

Yield of hexylsilane: 65% (from fractionation curve).

(Chloromethyl)silane H_3SiCH_2Cl

H_3SiCH_2Cl was prepared from 46 g of Cl_3SiCH_2Cl, 24 g of lithium hydride, and 95 ml of diisopentyl ether. The crude reaction product was collected in a trap.

Fractionation over LiH through a 35-plate column yielded 3.4 ml of H_3SiCH_2Cl, having the following constants: b.p. 30.5° (739 mm); d_4^{20} 0.9286; n_D^{20} 1.4157; found MR 21.76; calculated MR 22.01.

Found %: Cl 43.66; 43.36
Calculated %: Cl 44.01

Diethylsilane $(C_2H_5)_2SiH_2$

The substances taken for reaction were $(C_2H_5)_2Si(OC_2H_5)_2$ (41 g), LiH (13 g), and diisopentyl ether (50 ml). First a fraction of b.p. 54-56° was taken, and then a small amount of solvent came over. Fractionation through a 35-plate column yielded 7.7 ml (25%) of diethylsilane, b.p. 55.3° (757.5 mm); d_4^{20} 0.6849; n_D^{20} 1.3915. The literature [18] gives: b.p. 56° (741 mm); d_4^{20} 0.6843; n_D^{20} 1.3921.

SUMMARY

1. It has been shown for the first time that reduction by means of lithium hydride can be successfully extended to alkylhalosilanes and other classes of organosilicon compounds (alkenylhalosilanes, halo(haloalkyl)silanes, alkylethoxysilanes), and in the last case reduction proceeds selectively, without affecting the halogen of the haloalkyl group.

2. It has been shown that diallylsilane undergoes thiocyanation in almost theoretical yield, and that allylsilane combines with HCl in accordance with Markovnikov's rule.

3. The results provide data that characterize the dependence of the freezing points of some silanes on their structure. It has been shown also that the value of the refraction for the Si—C bond is determined by the radical containing the carbon attached to silicon. In particular, for allyl attached to silicon this value should be taken as 2.68 ml/mole.

Received July 17, 1953

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SYNTHESIS AND PROPERTIES OF (1-METHYLALLYL)- AND 2-BUTENYL-SILANES

A. D. Petrov, V. A. Ponomarenko, and V. I. Boikov

Unsaturated sila-hydrocarbons, being convenient starting materials for the synthesis of various derivatives and the preparation of polymers, are attracting much attention. The syntheses and properties have been described of vinyl- and allyl-silanes [1], (2-methylallyl)silanes, and other unsaturated silanes [2]. The synthesis of (1-methylallyl)- and 2-butenyl-silanes by the Grignard-Wurtz method with the aid of 1-halo-2-butenes is associated with the necessity for the investigation of the allyl rearrangement of the latter:

$$CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}X \rightleftharpoons CH_3{-}CH{=}CH{-}CH_2\cdot X,$$

for it cannot be predicted whether the process will be subject to exactly the same rules as those observed in the synthesis of hydrocarbons [3]. The most important of these rules is that the reaction will proceed by the scheme

$$[C_4H_7]MgX + R_1\cdot X \rightarrow CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot R_1 \qquad (1)$$

i.e., mainly in the direction of secondary forms, when the halogen compound capable of rearrangement is applied in the form $R\cdot MgX$, but, on the contrary, mainly in the direction of the formation of primary forms when the halogen compound capable of rearrangement is applied in the form RX, i.e., according to the scheme

$$[C_4H_7]\cdot X + R_1\cdot MgX \rightarrow CH_3{-}CH{=}CH{-}CH_2\cdot R_1. \qquad (2)$$

We have accordingly carried out, on the one hand, reactions of $[C_4H_7]MgBr$ with $(C_2H_5)_2SiCl$, CH_3SiHCl_2 and $SiCl_4$ and, on the other hand, the reaction of $(CH_3)_3SiCH_2MgCl$ with $[C_4H_7]Br$. It was found that in all cases these same rules were obeyed. In the establishment of the main directions of these reactions much help was obtained from the application of Raman spectra.

Since it was not found possible to separate the mixture of (1-methylallyl)- and 2-butenyl-silanes obtained by reaction of $[C_4H_7]MgBr$ with $(C_2H_5)_2SiCl$ by fractionation through a column owing to the closeness of their boiling points, we decided to obtain an idea of the composition of this mixture from a study of Raman spectra. A comparison of the spectrum of the product of the hydrogenation of this mixture with that of authentic butyltriethylsilane showed that the amount of the latter in this product did not exceed 10%, so that in this case the reaction went mainly in accordance with Equation 1.

The unsaturated sila-hydrocarbon formed by reaction of $(CH_3)_3SiCH_2MgCl$ with $[C_4H_7]Br$ gave a frequency of 1669 cm^{-1} and only traces of the frequencies 3000 cm^{-1} and 3078 cm^{-1} characteristic for a double bond at the end of the chain. This indicates that here the main reaction product is $(CH_3)_3Si{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_3$, i.e., the reaction proceeds in accordance with Equation 2.

When 2-butenylmagnesium bromide was treated with $SiCl_4$ and with CH_3SiHCl_2, chloro(1-methylallyl)silanes again predominated in the products. For the determination of the ratio of the 1-methylallyl and 2-butenyl compounds it was found to be expedient to reduce the halogens with lithium hydride, since this yielded isomers having a greater difference in boiling point. At the same time, this reduction permitted the synthesis of the silicon analogs of 3-methyl-1-butene, 2-pentene, and 3-methyl-1-pentene, having in each case one carbon atom replaced by silicon.

Among the chemical properties of this new type of alkenylsilanes (having hydrogen attached to silicon) is their ability to undergo thiocyanation, and the thiocyanogen numbers are only slightly higher than the calculated values when dilute solutions are used. The physical properties of these unsaturated sila-hydrocarbons are shown in juxtaposition with those of the corresponding olefins in the table.

Apart from the substances shown in the table, we have prepared and characterized the following: 1) triethyl(1-methylallyl)silane $(C_2H_5)_3Si{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH{=}CH_2$; 2) trichloro(1-methylallyl)silane $Cl_3Si{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH{=}CH_2$; 3) trimethyl-3-pentenylsilane $(CH_3)_3Si{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_3$; 4) sec-butyltriethylsilane $(C_2H_5)_3Si{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}CH_3$. The

Physical Properties of Olefins and Their Silicon Analogs

Compound	B.p. in °C (p in mm Hg)	d_4^{20}	n_D^{20}
$H_3C-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH=CH_2$ 3-Methyl-1-butene	20.1	0.6340	1.3677
$H_3Si-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH=CH_2$ (1-Methylallyl)silane	43 (750)	0.6846	1.4050
$H_3C-CH_2-CH=CH-CH_3$ 2-Pentene	36.5	0.6504	1.3793
$H_3Si-CH_2-CH=CH-CH_3$ 2-Butenylsilane	56.0-57.5	0.7042	1.4178
$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH=CH_2$ 3-Methyl-1-pentene	54	0.6700	1.3835
$CH_3-SiH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH=CH_2$ Methyl(1-methylallyl)silane	70-71 (749)	0.7165	1.4162

sila-hydrocarbons given in the table were prepared by the reduction of the corresponding halosilanes with LiH; the sila-hydrocarbon No. 4 was prepared by reduction of No. 1 with hydrogen in presence of Raney nickel.

It should be noted that, whereas $(C_2H_5)_3SiCl$ condensed with a Grignard reagent having an allyl-type radical with formation of sila-hydrocarbon No. 1 in 35% yield, the condensation of the same chloro compound under the same conditions with sec-butylmagnesium chloride did not go at all. $(CH_3)_3Si-CH_2Cl$ was prepared by the chlorination of CH_3SiCl_3 to give Cl_3SiCH_2Cl and the reaction of the latter with CH_3MgI. It was found that, not only $(CH_3)_3SiCH_2Cl$ (50% yield), but also $(CH_3)_3SiCH_2I$ was formed in appreciable amount (25.6% yield). The formation of this iodo compound is probably to be explained by the reaction:

$$(CH_3)_3SiCH_2Cl + MgClI \rightarrow MgCl_2 + (CH_3)_3SiCH_2I.$$

It is interesting to note also that the mixture of trichloro(1-methylallyl)- and 2-butenyltrichloro-silanes formed by the reaction

$$2BrMg[C_4H_7] + 2SiCl_4 \rightarrow Cl_3Si-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}\cdot CH=CH_2 + Cl_3Si-CH_2-CH=CH-CH_3$$

polymerizes fairly readily with heat (when distilled), possibly partly owing to the presence of dialkenylsilane impurities.

EXPERIMENTAL

C_4H_7Br. A mixture of 336 g of butadiene and 155 g of glacial acetic acid was saturated with HBr at −10°. The product was washed free from acid, dried, and fractionated; 563 g of the fraction of b.p. 85-102° was obtained.

$(C_2H_5)_3SiC_4H_7$. To 14 g of Mg in 600 ml of ether 10 g of C_4H_7Br was added to initiate reaction. A mixture of 62 g of $(C_2H_5)_3SiCl$ and 40 g of C_4H_7Br was added over a period of 3 hours 30 minutes. The ether was distilled off, and the contents of the flask were heated for six hours in a boiling water bath. Decomposition with water followed by fractionation through a 35-plate column yielded 22 g (35%) of $(C_2H_5)_3SiC_4H_7$, b.p. 185-188° (750 mm); d_4^{20} 0.7990; n_D^{20} 1.4504; found MR 57.33; calculated MR 57.59.

$(C_2H_5)_3SiC_4H_9$. With the object of determining its structure $(C_2H_5)_3SiC_4H_7$ (17.8 g) was hydrogenated in a 150-ml autoclave in presence of Raney nickel at 180° and initial hydrogen pressure of 80 atm. The hydrogenation product, isolated with the aid of a 35-plate column, had b.p. 190.5-191.5° (748.3 mm); d_4^{20} 0.7848; n_D^{20} 1.4383; found MR 57.68; calculated MR 58.06.

Found %: C 70.49; H 14.15; Si 15.55

$(C_2H_5)_3SiC_4H_9$. Calculated %: C 69.68; H 14.04; Si 16.28

For the purpose of the Raman analysis the synthesis of $(C_2H_5)_3Si(n\text{-}C_4H_9)$ was repeated, the properties of which, according to the literature [4], are b.p. 192°; d_4^{20} 0.7786; n_D^{20} 1.4348. Our preparation had b.p. 190.5° (741.1 mm); d_4^{20} 0.7797; n_D^{20} 1.4350.

An attempt to prepare sec-butyltriethylsilane (which has not been synthesized previously) under the same conditions (i.e., condensation of $(C_2H_5)_3SiCl$ with sec-butylmagnesium bromide, six hours, 80°) was not successful.

Raman spectra* were determined both for the hydrogenation product of $(C_2H_5)_3SiC_4H_7$, and for $(C_2H_5)_3Si(n\text{-}C_4H_9)$.

1. n-Butyltriethylsilane:

cm^{-1}: 149 (3), 261 (4b), 303 (3), 333 (1), 515 (2), 550 (3), 569 (8), 638 (4b), 724 (4b), 752 (4b), 849 (4), 882 (6), 974 (5b), 1013 (4b), 1051 (4), 1079 (3), 1191 (4), 1236 (5b), 1292 (1), 1304 (3), 1345 (1), 1385 (3), 1418 (5), 1448 (3), 1467 (8).

2. Mixture of hydrogenation products:

cm^{-1}: 150 (3), 262 (3), 297 (3), 521 (2), 548 (2), 568 (8), 638 (3), 722 (2b), 850 (4), 880 (4), 910 (1), 973 (6), 1012 (4b), 1021 (2), 1050 (1), 1054 (1b), 1188 (2b), 1214 (1), 1236 (5), 1312 (2), 1382 (3), 1419 (4), 1452 (2), 1467 (7).

The spectrum of n-butyltriethylsilane contains the following characteristic frequencies: 1) for the normal chain in butyl: 1051 (4), 1079 (3), 1345 (1), 1448 (3); 2) for the ethyl radical attached to Si: 974 (5b), 1013 (4), 1236 (5b), 1467 (8), as noted previously [5]. The spectrum of the mixture, however, contains only frequencies characteristic for the ethyl radical: 973 (6), 1012 (4b), 1236 (5) and 1467 (7); the frequencies for the normal chain are either very weak or absent altogether. In their place there appear the lines 1021 (2), 1094 (1b), 1188 (2b) and 1452 (2), which may belong only to a branched butyl radical attached to silicon.

On the basis of these considerations it follows that the mixture contained mainly sec-butyltriethylsilane, and only a small amount (up to 10%) of n-butyltriethylsilane.

$Cl_3SiC_4H_7$. A mixture of 500 g of $SiCl_4$ and 200 g of C_4H_7Br was added at the rate of 95-100 drops per minute to 72 g of Mg in 1500 ml of ether. The ether was distilled off, and the mixture was heated for five hours in a water bath. The reaction product was filtered from the precipitate, and the residual ether and excess of $SiCl_4$ were distilled off. As the reaction product had become very thick, indicating that polymerization was setting in, monomer was distilled off under reduced pressure (70 mm). A fraction (79 g) of b.p. 57-102° was obtained, and the residue was a thick mass of polymer. Fractionation of the fraction through a column (Fig. 1) yielded 47.8 g of main product, b.p. 137-138° (757.5 mm); d_4^{20} 1.2013; n_D^{20} 1.4524; found MR 42.60; calculated for $Cl_3SiC_4H_7$ MR 42.59.

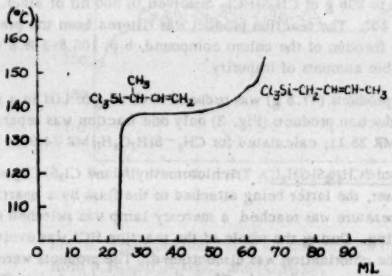

Fig. 1. Fractionation curve for the mixture of trichloro(1-methylallyl)- and 2-butenyltrichloro-silanes.

* The spectra were kindly determined by Yu. P. Egorov.

$H_3SiCHCH=CH_2$ and $H_3SiCH_2CH=CHCH_3$. To 18.2 g of LiH in 70 ml of diisopentyl ether, 47.8 g of $Cl_3SiC_4H_7$ (CH_3) was added. The reduction was carried out in a still incorporating a small rectification column under the conditions described previously [6]. In the receiver, which was surrounded with a mixture of acetone and dry ice, 11.3 g of $H_3SiC_4H_7$ was collected, and this was fractionated through a 35-plate column (Fig. 2).

Fraction I, b.p. 43° (750 mm) was $H_3Si-CH(CH_3)-CH=CH_2$; d_4^{20} 0.6846; n_D^{20} 1.4050; found MR 30.85; calculated for $H_3SiC_4H_7$ MR 30.79.

Fraction II, b.p. 56.0-57.5° (752 mm) was $H_3Si-CH_2-CH=CH-CH_3$; d_4^{20} 0.7042; n_D^{20} 1.4178; found MR 30.83; calculated MR 30.79.

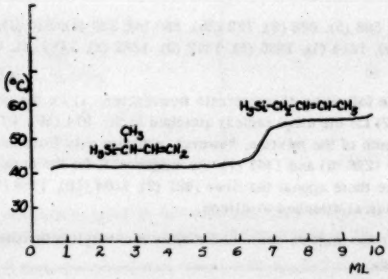

Fig. 2. Fractionation curve for the mixture of (1-methylallyl)- and 2-butenyl-silanes.

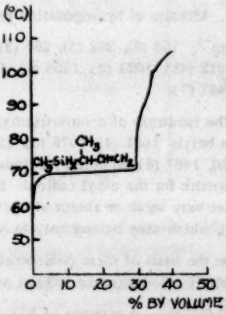

Fig. 3. Fractionation curve for methyl(1-methylallyl)silane.

$CH_3SiH(Cl)(C_4H_7)$ and $CH_3SiH_2-CH(CH_3)-CH=CH_2$. The Grignard reagent prepared from 40 g of Mg and 135 g of C_4H_7Br in 500 ml of ether was added to 206 g of CH_3SiHCl_2 dissolved in 300 ml of ether. The reaction was completed by heating in a water bath at 50°. The reaction product was filtered from the precipitate, and 118 g remained after removal of ether. The fraction of the chloro compound, b.p. 105.8-108.8°; d_4^{20} 0.8025; $n_D^{20.8}$ 1.4259, was separated; it contained appreciable amounts of impurity.

The wide fraction of reaction products (47.5 g) was reduced with 15 g of LiH in a medium of diisopentyl ether. In the fractionation of the reduction products (Fig. 3) only one fraction was separated: b.p. 70.0-71.0° (749 mm); d_4^{20} 0.7165; n_D^{20} 1.4162; found MR 35.11; calculated for $CH_3-SiH_2C_4H_7$; MR 34.96.

Cl_3SiCH_2Cl, $(CH_3)_2SiCH_2Cl$, and $(CH_3)_3SiCH_2I$. Trichloromethylsilane Cl_3SiCH_3 was placed in a flask fitted with thermometer and reflux condenser, the latter being attached to the flask by a quartz tube having a porcelain filling. When the final boiling temperature was reached, a mercury lamp was switched on, and chlorine was passed into the reaction zone above the filling. During the whole of the reaction HCl was evolved. When the boiling point of the product attained 110°, the chlorination was discontinued. The products were fractionated through a column. Altogether 532 g of CH_3SiCl_3 was chlorinated. The substances isolated were 227 g of $Cl_3SiCH_2 \cdot Cl$, 60 g of unchanged CH_3SiCl_3, and 208 g of residue. The yield of Cl_3SiCH_2Cl was 39% on the amount of CH_3SiCl_3 that reacted.

To 48.3 g of Mg in 600 ml of ether, 299.5 g of CH_3I was added, and to this Grignard reagent, 96 g of Cl_3SiCH_2Cl was then added. The contents of the flask were heated in a boiling water bath for seven hours. The 73 g of reaction products remaining after removal of ether was fractionated through a 35-plate column (Fig. 4), and yielded:

Fraction I, b.p. 97.0° (752 mm) was $(CH_3)_3Si \cdot CH_2 \cdot Cl$, 32 g; n_D^{20} 1.4172. For this chloro compound the literature [7] gives b.p. 97.1°; n_D^{19} 1.4180.

Fraction II, b.p. 139.5° was $(CH_3)_3SiCH_2I$, 28.5 g; n_D^{20} 1.4895. For this iodo compound the literature [7] gives b.p. 139.5° and n_D^{20} 1.4917.

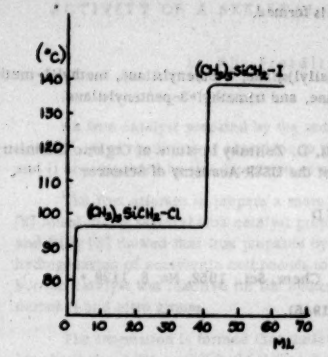

Fig. 4. Fractionation curve for the mixture of (chloromethyl)- and (iodomethyl)-trimethylsilanes.

$(CH_3)_2Si-CH_2-CH_2-CH=CH-CH_3$. To $(CH_3)_3SiCH_2MgCl$, prepared from 32 g of $(CH_3)_3SiCH_2Cl$ and 6.5 g of Mg in 100 ml of ether, 36 g of C_4H_7Br was added dropwise, under stirring.

Reaction was slow (slight rise in temperature). When the mixture was heated in a water bath, a very vigorous reaction set in, and part of the product was lost. The remaining 21.5 g was fractionated through a 35-plate column (Fig. 5), and two substances were isolated.

Fraction I was a sila-hydrocarbon of b.p. 139.8° (756.5 mm); d_4^{20} 0.7466; n_D^{20} 1.4235; found MR 48.58; calculated for $(CH_3)_3SiCH_2C_4H_7$ MR 48.35.

Found %: C 67.57; H 12.80; Si 19.56
$(CH_3)_3SiCH_2C_4H_7$. Calculated %: C 67.53; H 12.75; Si 19.72

In the Raman spectrum of the substance of b.p. 139.8°, the frequence 1669 (8) was found, and only traces of the frequencies 1642 (2), 3000 (2), 3078 (1), and others. According to a previous investigation by Egorov [2, 5], the frequencies 1642 (2), 3000 (2), and 3078 (1) correspond to II (below), the content of this form being not greater than 5% judging from the intensities. The frequency 1669 (8) corresponds to I, which greatly predominates in the fraction, its content being about 95%.

$(CH_3)_2Si-CH_2-CH_2-CH=CH-CH_3$; $(CH_3)_3SiCH_2-\underset{CH_3}{CH}-CH=CH_2$

(I) (II)

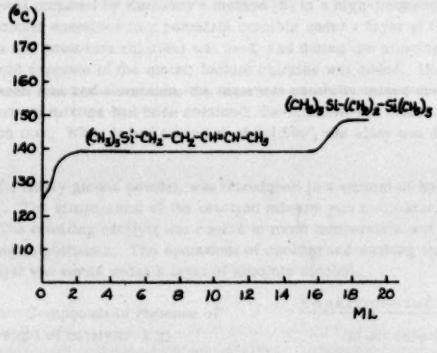

Fig. 5. Fractionation curve for the mixture of reaction products from $(CH_3)_3SiCH_2MgCl$ and $[C_4H_7]Br$.

Fraction II, b.p. 150°, was $(CH_3)_3Si-CH_2-CH_2-Si(CH_3)_3$; d_4^{20} 0.7566; n_D^{20} 1.4200; found MR 58.33; calculated for $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$: MR 58.43. For this sila-hydrocarbon, the literature [8] gives b.p. 150-151°; d_4^{20} 0.7536; n_D^{20} 1.4204.

SUMMARY

1. It has been shown that in the Grignard-Wurtz synthesis of alkenylsilanes from 1-bromo-2-butenes, the latter undergo the same type of allyl rearrangement as in the synthesis of hydrocarbons, i.e., in the condensation of R·MgX

(R = 2-butenyl) with R_1X (R_1 = $\equiv Si-X$), (1-methylallyl)silanes $\equiv Si-\underset{C}{\underset{|}{C}}-C=C$ are formed. When R·X is condensed with

R_1MgX (R_1 = $\equiv Si-CH_2MgX$), a 3-pentenylsilane $\equiv Si-C-C-C=C-C$ is formed.

2. Silicon analogs of olefins have been synthesized: (1-methylallyl)silane, 2-butenylsilane, methyl(1-methylallyl)silane, trichloro(1-methylallyl)silane, triethyl(1-methylallyl)silane, and trimethyl-3-pentenylsilane.

Received July 17, 1953

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* See Consultants Bureau Translation, page 989.

ACTIVITY OF A SKELETAL IRON CATALYST IN HYDROGENATION REACTIONS

L. Kh. Freidlin, K. G. Rudneva, and A. S. Sultanov

An iron catalyst prepared by the reduction of ferric oxide at 400-500° is of low activity for hydrogenation reactions [1]. Hydrogenation of acetylene in presence of this catalyst begins at 180°; it yields a mixture of hydrocarbons and is accompanied by the deposition of a carbonaceous film on the catalyst.

The first attempt to prepare a more active iron catalyst from an alloy was unsuccessful. Dupont and Piganiol [2] found that a skeletal iron catalyst prepared by the leaching of an iron-aluminum alloy was quite inactive. Paul and Hilly [3] showed that iron prepared by the leaching of an iron-aluminum alloy (20:80) at 80-90° catalyzed the hydrogenation of acetylenic compounds to ethylenic compounds by hydrogen at 100° under a pressure of 50 atm; but the catalyst was inactive for the hydrogenation of ethylenic compounds, nitriles, and compounds containing carbonyl and nitro groups.

The impression is formed that skeletal iron catalysts differ greatly in activity from skeletal nickel catalysts. We, however, have established [4] that the activity of a skeletal iron catalyst, like that of a nickel catalyst, is associated with the presence of hydrogen within it, i.e., the nature of the activity is similar. We showed also that an iron catalyst is more readily stripped of hydrogen and deactivated than a nickel catalyst. This suggested to us that the activity of a skeletal iron catalyst should be studied at a lower temperature, at which its active surface would be more stable. Our experiments have shown that this catalyst does, in fact, have a fairly high activity, and it can be used in much the same way as the nickel catalyst for the hydrogenation of many organic compounds at room temperature and normal pressure.

EXPERIMENTAL

Preparation of the Catalyst

An iron-aluminum alloy was prepared by Kurnakov's method [5] in a high-frequency furnace. Filings of Armco iron were added to melted aluminum contained in a porcelain crucible under a layer of slag. As a flux, a mixture of equal parts by weight of sodium and potassium chlorides was used, and during the alloying process, to reduce the volatility of the halides and avoid exposure of the metal, barium chloride was added. On account of the great difference in specific gravity between iron and aluminum, the mass was carefully mixed during the melting with a porcelain rod. When a homogeneous mixture had been obtained, the crucible was taken out of the furnace, and the melt was poured out onto an iron tray. When it had cooled to about 600°, the alloy was doused with cold water, and was then regarded as ready.

The alloy, in the form of a finely ground powder, was introduced in a current of hydrogen, into a 20% solution of sodium hydroxide at 60°. The temperature of the reaction mixture was maintained at not above 80° throughout the addition of the alloy. The resulting catalyst was cooled to room temperature and washed with distilled water until there was no reaction to phenolphthalein. The operations of cooling and washing were also carried out in a current of hydrogen. The catalyst was stored under a layer of absolute alcohol.

Hydrogenation of Various Organic Compounds in Presence of Skeletal Iron Catalyst at 20° (weight of catalyst: 1 g)

Substance hydrogenated	Amt. taken for reaction (g)	Hydrogen consumed (ml)	Degree of conversion (%)
Eugenol	0.3093	40.2	95
Phenyl vinyl ether	0.2495	46.7	100
Methyl methacrylate	0.3252	69.2	95
Styrene	0.2273	49.6	100
2-Methyl-5-hexen-3-yn-2-ol	0.1385	82.2	97
2-Butyne-1,4-diol	0.2174	112.0	99
Mesityl oxide	0.1755	39.7	98

Experimental Conditions

In all experiments the same sample of skeletal iron catalyst was used; it was prepared by the leaching of an alloy containing 66% of aluminum. The hydrogenation was carried out at 20° in a hydrogenation flask, 150 mm in length and 30 mm in diameter. The sweep of the shake was 10.5 cm, and the rate of shaking was not less than 700 oscillations per minute. These conditions were such as to ensure that the reaction occurred in the kinetic region. A mixture of 1 g of catalyst and 10 ml of alcohol was introduced into the

flask in a current of hydrogen, and was then given fifteen minutes to enable complete saturation with hydrogen to occur. A definite amount of the substance to be hydrogenated was then introduced in 5-10 ml of solvent, the shaker motor was switched on, and the rate of absorption of hydrogen was determined.

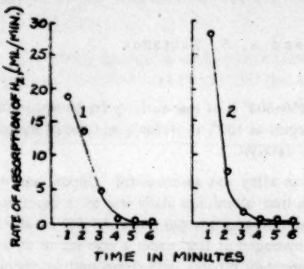

Fig. 1. Rate of hydrogenation of 0.3093 g of eugenol in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

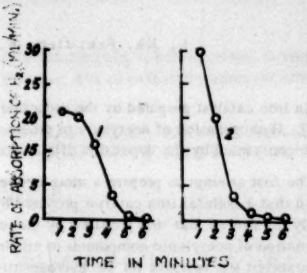

Fig. 2. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

Activity of Skeletal Iron Catalyst

For comparison purposes, in conjunction with the iron-catalyst experiments, studies were made of the activity of skeletal nickel catalyst in the same reactions and under analogous conditions. The nickel catalyst used was obtained by leaching a 50% Ni–Al alloy with 20% caustic soda at 105° for two hours. The relative activities of the iron and nickel catalysts were characterized by a comparison of the graphs showing the variation of the rate of hydrogen absorption with time for the hydrogenation of a definite weight of substance. The results of the experiments are given in the table and in Figures 1-9. The volume of hydrogen is always reduced to standard conditions.

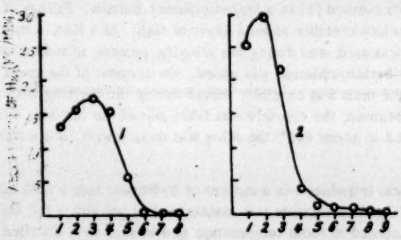

Fig. 3. Rate of hydrogenation of methyl methacrylate in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron, 0.3252 g of ester; 2) skeletal nickel, 0.4028 g of ester.

Fig. 4. Rate of hydrogenation of 0.2273 g of styrene in dioxane at 20° in presence of 1 g of skeletal iron catalyst.

Hydrogenation of Compounds Containing an Ethylene Bond

Figures 1, 2, 3, and 4 show the curves for the change in the rate of hydrogen absorption with time for the hydrogenation of four different compounds containing a double bond. It follows from the curves that eugenol, phenyl vinyl ether, methyl methacrylate, and styrene are hydrogenated rapidly, thus indicating the high activity of skeletal iron catalyst at 20° and normal pressure. The degree of hydrogenation of these compounds attains 95-100% of the theoretical value, and hydrogenation is complete in a few minutes. A comparison shows that the activity of an iron catalyst is quite of the same order as that of a skeletal nickel catalyst.

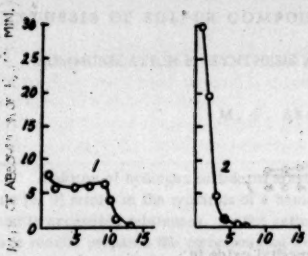

Fig. 5. Rate of hydrogenation of 0.0996 g of 2-methyl-3-butyn-2-ol in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

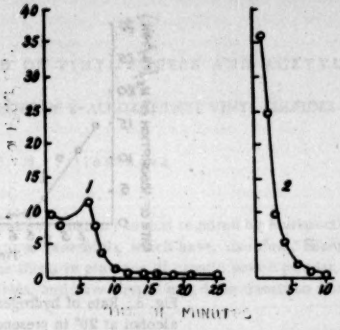

Fig. 6. Rate of hydrogenation of 0.1385 g of 2-methyl-5-hexen-3-yn-2-ol in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

Hydrogenation of Compounds Containing a Triple Bond

It will be seen from Figures 5, 6, and 7 that, unlike the curves for the nickel catalyst, those for the rate of hydrogenation in presence of skeletal iron have complicated forms. On the curve for the hydrogenation of 2-methyl-3-butyn-2-ol (Fig. 5), at the point corresponding approximately to 50% consumption of hydrogen, there is a break in the curve indicating a sharp fall in the rate of the process. The curve for the rate of hydrogenation of 2-methyl-5-hexen-3-yn-2-ol is similar in character (Fig. 6). On this curve the break occurs at a point corresponding to two-thirds of the total amount of hydrogen consumed. The curve for the hydrogenation of 2-butyne-1,4-diol is still more complex in form (Fig. 7); almost 50% of the hydrogen is absorbed at a constant rate, and there is then a definite rise in the rate of the process, which is followed finally by a fall.

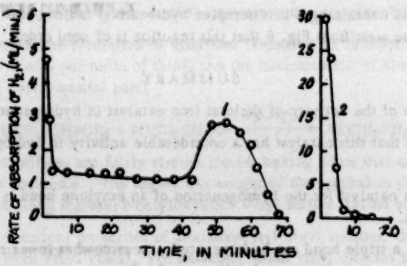

Fig. 7. Rate of hydrogenation of 0.2174 g of 2-butyne-1,4-diol in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

It follows from these results that for the hydrogenation of triple bonds skeletal iron catalyst again has a considerable activity, although it is somewhat lower than in the case of double bonds. There is a particularly marked difference in the rates of the process in presence of iron and nickel catalysts in the case of the hydrogenation of 2-butyne-1,4-diol.

Hydrogenation of Carbonyl Compounds

In the hydrogenation of mesityl oxide, the total consumption of hydrogen did not exceed the amount required for the hydrogenation of the double bond; it would appear that, under these conditions, the carbonyl group is not hydrogenated (Fig. 8).

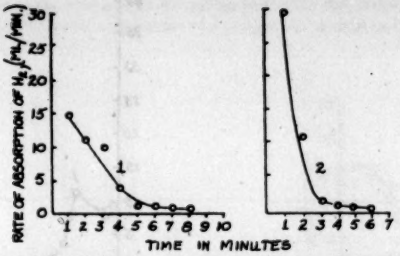

Fig. 8. Rate of hydrogenation of 0.1755 g of mesityl oxide in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

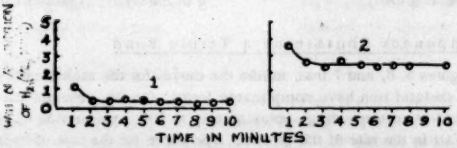

Fig. 9. Rate of hydrogenation of 0.1494 g of 2-butanone in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

In 2-butanone, a compound containing a less complex hydrocarbon radical, the carbonyl group is hydrogenated, although at a low rate. It will be seen from Fig. 9 that this reaction is of zero order.

SUMMARY

1. A study has been made of the activity of skeletal iron catalyst in hydrogenation reactions.

2. It has been established that this catalyst has a considerable activity in hydrogenation reactions at 20° and normal pressure.

3. The activity of an iron catalyst for the hydrogenation of an ethylene bond is two to three times less than that of a skeletal nickel catalyst.

4. Compounds containing a triple bond are hydrogenated at a somewhat lower rate than compounds containing an ethylene bond. A carbonyl group is hydrogenated still more slowly.

Received April 29, 1953

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SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS AND ACETYLENE

COMMUNICATION 9. SYNTHESIS AND CERTAIN PROPERTIES OF 2-ALKOXYETHYL VINYL SULFIDES

M. F. Shostakovsky and E. N. Prilezhaeva

Addition of hydrogen sulfide to alkyl vinyl ethers in the direction contrary to that required by Markovnikov's rule [1, 2] results in the synthesis of a homologous series of 2-alkoxyethanethiols, which have, therefore, become readily accessible substances. By the action of acetylene on these thiols in presence of caustic potash powder, we have readily prepared the corresponding 2-alkoxyethyl vinyl sulfides, and have thus effected the transition from vinyl ethers to these vinyl sulfides.

$$CH_2{=}CHOR + H_2S \xrightarrow{-O-O-} ROCH_2CH_2SH + CH{\equiv}CH \xrightarrow{KOH} ROCH_2CH_2SCH{=}CH_2. \quad (1)$$

Some unsubstituted vinyl sulfides have been described previously in patent specifications by Reppe and coworkers [3], who prepared them by the vinylation of thiols with acetylene diluted with nitrogen. In Soviet literature, an attempt has been described [4] to apply the method of vinylation developed for alcohols by Favorsky and Shostakovsky [5] (vinylation with acetylene without dilution with inert gases) to the synthesis of isopentyl vinyl sulfide. The author, however, first converted the 3-methylbutanethiol into its potassium derivative, which naturally yielded considerable amounts of diisopentyl sulfide, thus reducing the yield of the vinyl sulfide.

We have previously shown [6] that by slight modification of the Favorsky-Shostakovsky method it is possible to synthesize ethyl vinyl sulfide from ethanethiol in fairly good yield (about 50%), the only by-product being 1,2-bis(ethylthio)ethane:

$$C_2H_5SH + CH{\equiv}CH \xrightarrow[135\text{-}150^\circ]{5\%\ KOH} CH_2{=}CHSC_2H_5. \quad (2)$$

$$CH_2{=}CHSC_2H_5 + C_2H_5SH \rightarrow C_2H_5SCH_2CH_2SC_2H_5. \quad (3)$$

The extension of the use of these reaction conditions to 2-alkoxyethanethiols, which are of lower volatility and higher molecular weight, leads to the synthesis of the corresponding vinyl sulfides in 70-80% yield.

The secondary reaction, the formation of disulfides (Equation 4), is suppressed owing to the appreciable excess of acetylene (1.5-1.7 moles per mole of thiol) and the maintenance of almost complete absence of oxygen in the reaction medium (see experimental part)

$$ROCH_2CH_2SCH{=}CH_2 + ROCH_2CH_2SH \xrightarrow{-O-O-} ROCH_2CH_2SCH_2CH_2SCH_2CH_2OR. \quad (4)$$

2-Alkoxyethyl vinyl sulfides are fairly viscous liquids having odors that are somewhat improved by the presence of the alkoxy group in the molecule. The higher the weight of the radical in the alkoxy group, the more it suppresses the odor of the sulfur-containing residue; 2-octyloxyethyl vinyl sulfide has an odor similar to that of octyl alcohol.

In the study of the chemical properties of 2-alkoxyethyl vinyl sulfides, there were immediate indications of their essential difference from vinyl ethers. For example, these vinyl sulfides slowly polymerized in presence of air and diffuse light with formation of colorless, viscous liquid polymers. Chlorides, such as $FeCl_3$ and $SnCl_2$, which catalyze the polymerization of vinyl ethers [7], did not promote any appreciable polymerization in 2-butoxyethyl vinyl sulfide, either in the cold, or when heated in a sealed tube at 100° for 24 hours. On the other hand, according to preliminary trials, the presence of this sulfide suppresses the polymerization of butyl vinyl ether in presence of $FeCl_3$ to a considerable extent.

When 2-butoxyethyl vinyl sulfide and 2-butoxyethanethiol are brought together in the air, 1,2-bis(2-butoxyethylthio)ethane is formed quantitatively in accordance with Equation 4. Here the addition of thiol occurs exclusively contrary to Markovnikov's rule, which is different from the behavior of vinyl ethers: in presence of air these give mixtures of abnormal and normal addition products with thiols [8].

Introduction of sulfur in place of oxygen in the molecule of a vinyl ether evidently reduces the tendency for its double bond to undergo reactions having an ionic character and increases the probability of reactions of the free-radical type.

The action of mercuric chloride on 2-alkoxyethyl vinyl sulfides in an absolute ether medium results in the formation of a noncrystallizing viscous complex salt. A completely different reaction occurs in ethanol solution. In this case the thiol residue separates quantitatively as the mercurichloride, an equivalent amount of HCl is liberated, and an acetal is evidently formed in accord with the following overall equation:

$$ROCH_2CH_2SCH{=}CH_2 + HgCl_2 + 2C_2H_5OH \rightarrow ROCH_2CH_2SHgCl + HCl + CH_3CH(OC_2H_5)_2. \quad (5)$$

When an aqueous solution of mercuric chloride is used, acetaldehyde is formed. Hence, the alkylthio group in vinyl sulfides is split off just as readily by the action of mercuric chloride as in monothioacetals [9] and mercatals [9, 10]; the presence of alcohol or water is, however, necessary. Consideration of the mechanism of this process will be given later on the basis of supplementary experimental data. The reaction goes almost quantitatively; the titration of the hydrochloric acid that separates with 0.1 N NaOH in presence of Methyl orange can be used for the quantitative determination of the vinyl sulfide.

It is interesting that Davis and Oxford [11] obtained what they considered to be a complex salt of 2-ethoxyethyl vinyl sulfide by the action of mercuric chloride; it melted at 152-153°, but "did not give satisfactory analytical figures". The substance that they had actually obtained was 2-ethoxyethylthiomercury chloride $C_2H_5OCH_2CH_2SHgCl$, formed by Equation 5 (m.p. 154.5-155.5°).

Hence, the reaction of vinyl sulfides with mercury salts is again essentially different from the corresponding reaction of vinyl ethers. As Nesmeyanov, Lutsenko, and Vereshchagina showed [12], mercury salts add at the double bond of a vinyl ether, the final product being mercurated acetaldehyde. In vinyl sulfides the action of the mercury salt is apparently directed to the second reaction center, the sulfur atom.

EXPERIMENTAL

Synthesis of 2-Alkoxyethyl Vinyl Sulfides

The preparation of the thiols used in the synthesis of 2-alkoxyethyl vinyl sulfides has been described in previous communications [1, 2]. These thiols had the following physical constants (Table 1):

TABLE 1

Properties of 2-Alkoxyethanethiols $ROCH_2CH_2SH$

R	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
C_2H_5	126-128 (760)	1.4456	0.9412
p-C_3H_7	64 (40)	1.4478	0.9227
i-C_3H_7	56.1-56.4 (44)	1.4424	0.9136
p-C_4H_9	48 (6)	1.4488	0.9111
i-C_4H_9	45.2-45.5 (9)	1.4444	0.9038
i-C_5H_{11}	53.9-54.5 (6)	1.4489	0.9028
p-C_8H_{17}	103 (4.5)	1.4556	0.8906
C_6H_{11} (cyclohexyl)	73-73.5 (4.5)	1.4864	0.9938

All vinylation reactions were carried out in horizontal stainless steel rotating autoclaves. The thiols were freshly distilled for the vinylations. In all experiments the amount of KOH powder taken was 5% on the weight of the thiol. The weight of thiol was chosen so that there would be a considerable excess of acetylene when the autoclave was filled only once with this gas during the experiment. The KOH and thiol were introduced into the autoclave, and the gases present were displaced by acetylene. Acetylene was then passed into the autoclave, and heating was commenced. The temperature was maintained within the range 135-150°, for 1.2-2.0 hours for small loads (0.15-liter autoclave) and 2-2.5 hours for large loads (0.5-2.5-liter autoclaves). After cooling, the reaction mixture was left until the next day. The excess of acetylene was liberated, and the reaction products were washed into a flask with a small amount of dry ether. The vinyl sulfides were isolated by vacuum distillation; in the first fractionation they came over within a range of 2-3°, and when redistilled their constants were unaffected. The yields of products, as obtained in the first fractionation, are given in Table 2. In all of the experiments there were very small amounts of dark-colored residue, which were not investigated in the experiments with small amounts of starting materials. Experiments on the vinylation of larger amounts of 2-butoxyethanethiol (Expts. No. 6 and 7) showed that, in addition to resin, these residues contained some disulfides, formed by Equation 4.

It will be seen from Table 2 that for a good yield an excess of acetylene is essential (1.5-1.8 moles per mole of thiol). The change from small amounts of thiol (Expts. No. 1-5 and 8-13) to large amounts (Expts. No. 6 and 7) is naturally accompanied by increase in the yield of vinyl sulfide (from 60-70% to 80-83%).

The results in Table 2 indicate how greatly any variation from the established procedure can affect the yield of sulfide. In Expt. No. 3, for example, the air in the autoclave was not displaced by acetylene before the vinylation, and this resulted in a great reduction in the yield of vinyl sulfide (to 53%) and in a rise in the amount of high-boiling residue. In this experiment, distillation of the residue yielded 1.8 g of a substance of b.p. 160-166° (6 mm),

TABLE 2

Conditions of the Synthesis of the Sulfides $ROCH_2CH_2SCH=CH_2$ from the Thiols $ROCH_2CH_2SH$

Expt. No.	R	Amt. of thiol taken (g)	Capacity of autoclave (liters)	C_2H_2 (moles per mole of thiol)	Duration of heating (hr)	Yield of sulfide (%)	Weight of resinous residue (g)
1	C_2H_5	8.0	0.15	1.4	1.0	60.0	~2
2	C_2H_5	6.5	0.15	1.7	2.0	71.6	<1
3	p-C_3H_7	9.5	0.15	1.7	1.5	52.8	3
4	p-C_3H_7	9.5	0.15	1.3	1.5	68.1	<1
5	i-C_3H_7	9.5	0.15	1.7	1.2	73.6	<1
6	p-C_4H_9	30.0	0.5	1.8	2.5	80.5	2.7
7	p-C_4H_9	154.5	2.5	1.6	2.5	83.2	10.4
8	i-C_4H_9	11.	0.15	1.6	2.0	71.3	<1
9	i-C_5H_{11}	12.0	0.15	1.0	1.0	61.7	2
10	i-C_5H_{11}	7.3	0.15	1.7	2.0	81.1	<1
11	p-C_8H_{17}	15.3	0.15	1.7	1.5	73.6	<1
12	C_6H_{11} (cyclohexyl)	11.2	0.15	1.3	2.0	41.4	3
13	C_6H_{11} (cyclohexyl)	9.8	0.15	1.7	1.5	70.1	~1

evidently the disulfide p-$C_3H_7OCH_2CH_2SCH_2CH_2SCH_2CH_2OC_3H_7$-p. In all of the other experiments the air was carefully displaced by acetylene.

In Expts. No. 1 and 9, the low yield is to be explained by the insufficiently long period of heating and by the inadequate amount of acetylene present in the reaction medium (particularly in Expt. No. 9). The removal of these defects greatly increased the yield (Expts. No. 2 and 10). In Expt. No. 12, the low yield is to be explained by the fact that during the vinylation the temperature of the reaction mixture was allowed to rise to 180°. In this case, in addition to the product indicated in the table, 1.4 g of cyclohexanol was obtained (b.p. 47.5-50° (6 mm); n_D^{20} 1.4380; d_4^{20} 0.9478; the literature [13] gives b.p. 160.5° (758 mm); n_D^{20} 1.4350; d_4^{20} 0.9471). This alcohol was evidently formed by breakdown of the original thiol. In Expt. No. 13 standard reaction conditions were observed, and the yield of sulfide was not lower than for the other thiols. In this experiment no cyclohexanol was obtained.

2-Alkoxyethyl vinyl sulfides are colorless liquids that may be distilled under reduced pressure without decomposition or resinification; when stored in the air, they slowly polymerize with rise in refractive index. The physical properties and analyses of these sulfides are given in Table 3. The specific gravity and refractive index slowly fall as the alkoxy group becomes larger or more branched. The whole series of these substances has a small, but definite, systematic exaltation of molecular refraction (+ 0.2 to + 0.4).

Addition of 2-Butoxyethanethiol to 2-Butoxyethyl Vinyl Sulfide

$$C_4H_9OCH_2CH_2SH + C_4H_9OCH_2CH_2SCH=CH_2 \rightarrow C_4H_9OCH_2CH_2SCH_2CH_2SCH_2CH_2OC_4H_9$$

The sulfide (62.5 g; b.p. 74-75°/6 mm) was mixed with the thiol (70.0 g; b.p. 48-49°/6.5 mm) in a conical flask (1.3 moles of the thiol to one mole of the sulfide). After ten minutes the temperature began to rise rapidly; it attained 75°, and then fell just as rapidly. The mixture was set aside overnight. Vacuum fractionation (3.1 mm) yielded the following fractions:

Fraction I, b.p. 39-41°, 16.0 g; n_D^{20} 1.4489;

Fraction II, b.p. 41-174°, 0.12 g;

Fraction III, b.p. 174-176°, 110.0 g; n_D^{20} 1.4870.

Fraction I was excess of thiol.

After refractionation, Fraction III came over completely at 175-175.5° (3.2 mm) and had n_D^{20} 1.4869; d_4^{20} 0.9778; calculated MR 86.04; found MR 86.61.

	Found %	C 57.31; 57.20;	H 10.37, 10.31;	S 21.76, 21.86
$C_{14}H_{30}O_2S_2$.	Calculated %	C 57.09;	H 10.27;	S 21.77

The product gave no red coloration with Methyl Orange after addition of excess of an alcoholic solution of mercuric chloride. It may, therefore, be concluded that it consisted of the pure sulfide:

TABLE 3

Properties of 2-Alkoxyethyl Vinyl Sulfides $ROCH_2CH_2SCH{=}CH_2$

No.	R	B.p. in °C (p in mm Hg)	d_4^{20}	n_D^{20}	MR		Composition					
					found	calculated	found			calculated		
							C%	H%	S%	C%	H%	S%
1	C_2H_5*	59.5-60 (14)	0.9475	1.4760	39.38	39.12	54.08 54.37	9.27 9.15	24.06 23.98	54.50	9.14	24.25
2	p-C_3H_7	45 (3)	0.9309	1.4750	44.17	43.74	57.64 57.62	9.72 9.79	21.66 21.54	57.48	9.65	21.92
3	i-C_3H_7	51.6-51.8 (7)	0.9258	1.4684	43.94	43.74	–	–	22.11 22.01	–	–	21.92
4	p-C_4H_9	72.4-72.8 (5)	0.9232	1.4721	48.50	48.36	59.79 59.68	10.14 10.09	20.14 20.18	59.94	10.07	20.02
5	i-C_4H_9	69.5 (6.5)	0.9139	1.4678	48.68	48.36	–	–	20.08 20.19	–	–	20.02
6	i-C_5H_{11}	72.2-72.5 (4)	0.9115	1.4691	53.26	52.98	61.89 61.86	10.41 10.43	18.46 18.24	62.01	10.41	18.40
7	p-C_8H_{17}	106.6-107.1 (2)	0.9006	1.4709	67.12	66.83	–	–	14.76 14.94	–	–	14.82
8	C_6H_{11} (cyclohexyl)	98.5-99 (4)	0.9942	1.5025	55.38	55.39	64.36 64.53	9.68 9.65	17.26 17.41	64.47	9.74	17.21

* According to the results of Davis and Oxford [11], 2-ethoxyethyl vinyl sulfide has b.p. 65° (8 mm) and d_4^{20} 0.9532. The nonagreement of these constants with ours is evidently to be explained by the fact that Davis and Oxford were dealing with an insufficiently pure substance, for they isolated this sulfide from a complex mixture obtained by the hydrolysis of bis(2-chloroethyl) sulfide with KOH in an aqueous-alcoholic medium. These authors state that the sulfide darkens with keeping; we did not observe this. No other sulfides of this series have been described in the literature.

$C_4H_9OCH_2CH_2SCH_2CH_2SCH_2CH_2OC_4H_9$,

and did not contain any of the isomeric mercaptal $CH_3CH(SCH_2CH_2OC_4H_9)_2$, which, as we in collaboration with Shapiro [9] have already shown, behaves like other mercaptals [10] and gives the mercurichloride of the thiol and HCl when treated with mercuric chloride.

Hence, the thiol adds to the vinyl sulfide entirely in the direction contrary to Markovnikov's rule (yield 95.8% on the amount of sulfide taken).

When the disulfide $(C_4H_9OCH_2CH_2SCH_2-)_2$ was treated with an equimolecular amount of mercuric chloride in ethanol, a noncrystallizing alcohol-insoluble oil was precipitated; it was not investigated further. After the addition of a considerable excess of ethanolic mercuric chloride (more than two moles per mole of sulfide), an oil was precipitated, and this gradually solidified when rubbed with a rod. Recrystallization from a small amount of boiling alcohol and drying in a vacuum desiccator yielded white crystals, m.p. 68.5-69°. Analysis indicated the formation of a complex salt with two molecules of mercuric chloride:

$$C_4H_9OCH_2CH_2\underset{\displaystyle HgCl_2}{S}CH_2CH_2\underset{\displaystyle HgCl_2}{S}CH_2CH_2OC_4H_9.$$

$C_{14}H_{30}O_2S_2 \cdot 2HgCl_2$. Found %: C 20.34; 20.29; H 3.66; 3.73
Calculated %: C 20.08; H 3.78

Reaction of 2-Alkoxyethyl Vinyl Sulfides with Mercuric Chloride in Ethanol Solution

A weighed amount of the vinyl sulfide was transferred from a small dropping bottle to a 50-ml flask having a ground-in stopper. A 20% solution of $HgCl_2$ in ethanol was then added from a buret in a two- to three-fold excess over that required by Equation 5. The mercurichloride began to be precipitated after 15-20 minutes. It was found that it was necessary to leave the reaction mixture for one day in order to ensure completion of reaction. It was then titrated with 0.1 N NaOH with Methyl orange as indicator (20 ml of water was first added). The transition from the pink to the yellow color is fairly sharp. Completion of reaction is indicated by the nonreturn of the pink color of the indicator after the end of the titration. If the titration is performed within two or three hours of the mixing of the reactants, the color returns and the titration does not give quantitative results.

TABLE 4

Quantitative Determination of Vinyl Sulfides $ROCH_2CH_2SCH=CH_2$

R	Sulfide found (% of theoretical amount)	
C_2H_5	98.9;	97.5
p-C_3H_7	99.5;	100.0
i-C_3H_7	98.7;	98.2
p-C_4H_9	100.0;	99.9
i-C_4H_9	99.1;	98.9
i-C_5H_{11}	97.5;	98.1
p-C_6H_{11}	100.3;	100.1
C_6H_{11} (cyclohexyl)	98.8;	99.1

It will be seen from Table 4 that such a method of titration permits vinyl sulfides to be quantitatively determined in presence of other substances (so long as these do not react with HCl and do not yield HCl when treated with mercuric chloride). On the average, the results are accurate within 1%.

Table 5 shows the weights of precipitate and the melting points of the alkoxyethylthiomercury chlorides formed by the precipitation of weighed amounts of the corresponding sulfide with mercuric chloride. These melting points agree with those of the mercurichlorides obtained by us in collaboration with Shapiro from the corresponding 2-alkoxyethanethiols [1, 2]. There was no depression in mixture melting points of the mercurichlorides obtained by the two methods. The results in Tables 4 and 5 confirm that the reactions of vinyl sulfides with mercuric chloride in ethanol go quantitatively in accordance with Equation 5.

Decomposition of 2-Butoxyethyl Vinyl Sulfide with Mercuric Chloride in Aqueous Solution

$$C_4H_9OCH_2CH_2SCH=CH_2 + HgCl_2 + H_2O \rightarrow C_4H_9OCH_2CH_2SHgCl + HCl + CH_3CHO$$

A mixture of 15 g of mercuric chloride, 2.6 g of $BaCO_3$, and 20 ml of water was placed in a flask fitted with reflux condenser and tube for passage of gas, and 4.0 g of 2-butoxyethyl vinyl sulfide was added; the mixture became slightly warm. The mixture was heated at a gentle boil in a slow current of nitrogen for 40 minutes. The acetaldehyde liberated was trapped in two traps, filled with ethanol and cooled with snow and salt. Toward the end of the heating, the precipitate became slightly yellow. The contents of the traps, which smelled strongly of acetaldehyde, were transferred to a measuring flask, diluted with water, and titrated by Ripper's method [15]. The amount of acetaldehyde found by titration was 0.45 g, and the amount calculated theoretically was 1.1 g, so that we succeeded in trapping only 40-45% of the acetaldehyde.

TABLE 5

Melting Points and Yields of the Mercurichlorides $ROCH_2CH_2SHgCl$

R	Amt. of sulfide taken (g)	Yield of mercurichloride (g)*		M.p. of the mercurichloride (°C)**	
		found	calculated	from sulfide	from thiol [1, 2]
C_2H_5	0.6	1.86	1.55	154-155***	154.5-155.5
p-C_3H_7	0.8	1.85	1.94	138.5	137-137.5
i-C_3H_7	0.54	1.73	1.31	154-154.5	153-153.5
p-C_4H_9	0.41	1.02	0.94	136.5-137.5	137.5-138
i-C_4H_9	0.5	0.98	1.15	143.5	144-144.5
i-C_5H_{11}	0.66	1.85	1.45	126-127	126
p-C_6H_{17}	0.9	1.57	1.76	125-127	126
C_6H_{11} (cyclohexyl)	0.5	1.20	1.06	151	150.5

* The yield refers to the precipitate before recrystallization; it was filtered from the excess of mercuric chloride solution two or three days after the precipitation, washed with cold alcohol on a glass filter, and dried to constant weight in a vacuum desiccator.

** The melting points are those of the twice recrystallized mercurichlorides (from boiling ethanol). After a single recrystallization, the melting range was rather wide and an opaque liquid was formed.

*** This mercurichloride has been prepared previously from the corresponding thiol by Swallen and Boord [14] (m.p. 152-153.5°), and also, it would appear, from 2-ethoxyethyl vinyl sulfide by Davis and Oxford [11] (m.p. 152-153°).

Polymerization of 2-Butoxyethyl Vinyl Sulfide with Storage

When 2-butoxyethyl vinyl sulfide is stored, its refractive index slowly rises. For example, after being stored for 2.5 months in a flask with a ground-in stopper, the sulfide had n_D^{20} 1.4746, instead of the original value, 1.4721. Distillation of 16 g of this product yielded 14 g of the pure sulfide, b.p. 55° (2 mm) and n_D^{20} 1.4720. The residue was colorless and of the consistency of glycerol; it had n_D^{20} 1.5048 and weighted 1.9 g. In another case, the sulfide, after being stored for five months in a sealed tube, had n_D^{20} 1.4768. Distillation of 26.4 g yielded 21.6 g of monomeric sulfide, b.p. 62-63.5° (3 mm) and n_D^{20} 1.4721. The colorless viscous residue had n_D^{20} 1.5055 and weighed 4.0 g.

The polymers were transferred to a wide beaker and dried in a vacuum desiccator at 130-140° to constant weight; they became slightly yellow under this treatment.

	Found %:	C 59.83; 59.84; H 10.07, 10.10; S 20.04, 20.41
$(C_6H_{12}OS)_p$.	Calculated %:	C 59.92; H 10.07; S 20.02

The molecular weight of these polymers, determined by the cryoscopical method in benzene, was 2500-3000 (degree of polymerization about 20).

When 2-butoxyethyl vinyl sulfide that has been distilled in a current of nitrogen is stored in the dark in a sealed tube previously filled with nitrogen, no polymer formation is observed, even after six months. This vinyl sulfide, therefore, unlike vinyl ethers, tends to undergo slow polymerization under the action of light and oxygen.

All of the microanalyses for the present investigation and for those of the preceding communications [1, 2, 8, 9] were carried out in the Microanalysis Laboratory of the Institute of Organic Chemistry of the USSR Academy of Sciences by the method of simultaneous determination of C, H, and S developed in that laboratory by Korshun and Sheveleva [16].

SUMMARY

1. A method is given for the synthesis of 2-alkoxyethyl vinyl sulfides from 2-alkoxyethanethiols in 70-80% yield.

2. A method is proposed for the quantitative determination of vinyl sulfides; it is based on the decomposition reaction occurring in presence of mercuric chloride.

3. A study of some of the chemical properties of 2-alkoxyethyl vinyl sulfides shows that vinyl sulfides differ greatly from their oxygen analogs in their reactions.

Received February 10, 1953

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SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS AND ACETYLENE

COMMUNICATION 10. SYNTHESIS AND CERTAIN REACTIONS OF ETHYL VINYL SULFIDE

M. F. Shostakovsky, E. N. Prilezhaeva, and N. I. Uvarova

It has been shown previously that a satisfactory method for the preparation of vinyl sulfides, including ethyl vinyl sulfide, is the vinylation of thiols under the reaction conditions of Favorsky and Shostakovsky [1, 2]:

$$RSH + CH{\equiv}CH \xrightarrow[135\text{-}150^\circ]{5\%\ KOH} RSCH{=}CH_2. \quad (1)$$

The vinylation of thiols must be effected in presence of a considerable excess of acetylene in order to reduce the probability of the occurrence of a secondary reaction between the alkyl vinyl sulfide formed and the thiol (by Equation 2):

$$RSCH{=}CH_2 + RSH \rightarrow RSCH_2CH_2SR. \quad (2)$$

Ethyl vinyl sulfide has been synthesized also by the reaction of vinyl bromide with the alkali-metal derivatives of ethanethiol in alcoholic solution [3, 4] and by the dehydration of 2-mercaptoethanol, prepared by the action of ethylene oxide on ethanethiol [5]. By the reaction of hydrogen sulfide with acetylene in presence of polysulfide catalysts [6], a mixture of ethyl vinyl sulfide, ethanethiol, and 1,2-bis(ethylthio)ethane has been obtained. By the action of acetylene diluted with nitrogen on ethanethiol in presence of alkaline catalysts, Reppe [7, 8] and coworkers have obtained ethyl vinyl sulfide (Equation 1) and 1,2-bis(ethylthio)ethane (Equation 2) in the molar ratio of 2:3.

Some of the methods cited above are described only in the patent literature [5, 6, 7]; others give poor yields (about 20-25%) [3, 4].

The object of the present investigation was the study of the chemical transformations of ethyl vinyl sulfide, and also the improvement of the method of synthesis by the reaction of Favorsky and Shostakovsky. For this purpose we first studied the nature of the above-mentioned secondary process, the example taken being the reaction between ethanethiol and ethyl vinyl sulfide, which results in the formation of 1,2-bis(ethylthio)ethane (Equation 2). It was shown that, if ethanethiol and acetylene are brought together under vinylation conditions in the molar ratio 2:1, the disulfide is the only reaction product. Thus, in spite of Reppe's assertion [8], an alkaline catalyst cannot prevent reaction between the thiol and the vinyl sulfide. The experiment cited shows that this reaction is rapid and quantitative in presence of air or traces of oxygen, and is suppressed by the antioxidant hydroquinone, i.e., shows the typical properties of free-radical processes. Addition of hydroquinone to the reaction mixture does in fact permit the yield of disulfide to be greatly reduced, and it enables the vinylation to be carried out by means of repeated doses of acetylene (as in the case of alcohols). In presence of air, 1,2-bis(ethylthio)ethane is the sole product of the reaction of ethyl vinyl sulfide with ethanethiol, whereas under these conditions ethyl vinyl ether gives a mixture of products of addition according to and contrary to Markovnikov's rule [9]:

$$CH_2{=}CHOC_2H_5 + C_2H_5SH \begin{cases} \rightarrow C_2H_5SCH_2CH_2OC_2H_5 \\ \rightarrow CH_3CH(OC_2H_5)_2. \end{cases} \quad (3)$$

The nature of the reaction between ethanethiol and ethyl vinyl sulfide enables us, therefore, to conclude that the latter has a higher tendency to undergo free-radical processes than its oxygen analog. This conclusion is confirmed also by a study of the reaction of ethyl vinyl sulfide with hydrogen sulfide. In the presence of traces of oxygen, i.e., under the conditions that have been used previously for this reaction [10], the addition of hydrogen sulfide goes readily and quantitatively, and yields products formed entirely in the direction contrary to Markovnikov's rule:

$$CH_2{=}CHSC_2H_5 + H_2S \rightarrow C_2H_5SCH_2CH_2SH; \quad (4)$$

$$C_2H_5SCH_2CH_2SH + C_2H_5SCH{=}CH_2 \rightarrow \begin{matrix} C_2H_5SCH_2CH_2 \\ \\ C_2H_5SCH_2CH_2 \end{matrix} \!\!> S \quad (5)$$

Ethyl vinyl sulfide polymerizes under the action of sunlight and 2,2'-azobis(2-methylpropionitrile), i.e., again under the conditions favoring free-radical processes. At the same time, its polymerization is not promoted by ionic catalysts, such as $SnCl_4$ and $FeCl_3$, in presence of which ethyl vinyl ether gives a high yield of polymer.

The reaction of ethyl vinyl sulfide with mercuric chloride in water and alcohol is also different from that of its oxygen analog, which combines with mercury salts at the double bond [13]. With mercuric chloride in aqueous or alcoholic solution, the vinyl sulfide loses its ethylthio group, which forms ethylthiomercury chloride:

$$CH_2{=}CHSC_2H_5 + HgCl_2 + 2C_2H_5OH \rightarrow C_2H_5SHgCl + HCl + CH_3CH(OC_2H_5)_2. \quad (6)$$

$$CH_2{=}CHSC_2H_5 + HgCl_2 + H_2O \rightarrow C_2H_5SHgCl + HCl + CH_3CHO. \quad [7]$$

It has been shown previously [2] that this reaction proceeds so quantitatively in ethanol that it can be used for the titrometric determination of vinyl sulfides.

In order to make an approach to an understanding of this interesting reaction, we studied it in a solvent medium that was unable to add at the double bond of the sulfide. For this purpose we selected diethyl ether.

Under these conditions an unstable complex salt (approximate composition $4HgCl_2 \cdot 3CH_2{=}CHSC_2H_5$), was isolated; it was rapidly decomposed by alcohol and water with formation of acetaldehyde, hydrogen chloride, and ethylthiomercury chloride. Although this decomposition reaction was far from quantitative, its products nevertheless enable us to suppose that an analogous salt of thionium structure is the first product of the reaction of mercuric chloride with the vinyl sulfide in an ethanol or water medium.

It will be clear from the above that vinyl sulfides differ from their oxygen analogs in showing a much higher tendency to undergo addition in the direction contrary to Markovnikov's rule. On the basis of our experimental results, however, it may be asserted that in certain reactions ethyl vinyl sulfide shows a close analogy to ethyl vinyl ether. Thus, catalytic quantities of sulfur dioxide enable us, as in the case of vinyl ethers [9], to direct the addition of ethanethiol to the vinyl sulfide mainly in accordance with Markovnikov's rule, with formation of 1,1-bis-(ethylthio)ethane:

$$CH_2{=}CHSC_2H_5 + C_2H_5SH \rightarrow CH_3CH(SC_2H_5)_2. \quad (8)$$

Vinyl sulfides, therefore, like vinyl ethers, can show dual reactivity, reacting by the ionic mechanism in accordance with Markovnikov's rule, and by the free-radical mechanism, in violation of the rule [11]. In no case, therefore, can they be assigned (as is done in a review article by Knunyants and Fokin [14]) to the group of substances of the type of vinyl ketones, alkenyl sulfones, and other substances that always unite with a negative grouping at the end carbon atom of the vinyl group.

EXPERIMENTAL

I. Synthesis of Ethyl Vinyl Sulfide

The synthesis of ethyl vinyl sulfide was carried out, under the conditions described in previous communications [1, 2], by vinylation of the thiol with acetylene in presence of 5% KOH. The results of a series of experiments are given in Table 1.

TABLE 1

Conditions of Synthesis of Ethyl Vinyl Sulfide

Expt. No.	Amt. of thiol taken (g)	Capacity of autoclave (liters)	Amt. of acetylene* (moles per mole of thiol)	Temperature of reaction (°C)	Duration of heating (hr)	Yield of ethyl vinyl sulfide (%)	Yield of 1,2-bis-(ethylthio)ethane
1	72.5	2.5	1.3	135-150	2.5	61.3	12.5
2	67.5	2.5	1.34	135-150	2.5	61.0	11.4
3	12.3	0.15	0.5	135-150	1.25	—	82.4
4	14.5	0.15	0.5·3	150-160	1.25·3	56.0	14.8

* In Expts. No. 1-3, one dose of acetylene was given, but in Expt. No. 4 hydroquinone was added and three doses of acetylene were given, each being followed by heating of the autoclave and then cooling.

Expts. No. 1 and 2 were carried out with an excess of acetylene, and the main reaction product was, therefore, ethyl vinyl sulfide. Expt. No. 3 was carried out with a deficiency of acetylene, and, as a result, only 1,2-bis(ethylthio)ethane was isolated (the product of the reaction in accordance with Equation 2 of the ethyl vinyl sulfide formed with the excess of thiol). In Expt. No. 4, 1.3 g of hydroquinone (5 mole-%) was added, and this permitted a number of doses of acetylene to be given (three portions of 0.5 mole each of acetylene per mole of thiol). The addition of hydroquinone retarded the addition of ethanethiol to ethyl vinyl sulfide. However, owing to an appreciable amount of resinification (possibly associated with the high reaction temperature) the yield of vinyl sulfide was no better than that obtained in Expts. No. 1 and 2. By way of example, we shall describe one experiment.

Expt. No. 1. For the vinylation, 72.5 g of ethanethiol, b.p. 34-35°, and 3.6 g of KOH powder were taken. The initial acetylene pressure was 13 atm, i.e., there was 39 g in the autoclave (or 1.3 moles of acetylene per mole of thiol). The reaction mixture was heated at 135-150° for 2 hours 30 minutes, and at the end of the experiment it was washed out into a flask with dry ether (300 ml) and dried over calcined Na_2SO_4. The ether was driven off from a Favorsky flask, but not completely, owing to the high volatility of ethyl vinyl sulfide. The reaction mixture, together with a small amount of ether, was then fractionated through a 20-plate column, the following fractions being obtained:

Fraction I, b.p. 35-91.5° (750 mm); 5 g; n_D^{20} 1.4680

Fraction II, b.p. 91.5-91.8 (750 mm); 63.3 g; n_D^{20} 1.4760

Resinous residue, 15.4 g

Fraction I, in addition to diethyl ether, contained some moist ethyl vinyl sulfide. Fraction II was ethyl vinyl sulfide, obtained in 61.3% yield. The ethyl vinyl sulfide content of this fraction was determined by titration in accordance with Equation 6, and was found to be 99.4, 99.6%. This method of isolation increased the yield of sulfide boiling over a range of 0.1-0.3° from 40-47% [1] to 61%.

Ethyl vinyl sulfide has a boiling point (corrected to 760 mm) of 91.9-92.2°; $\frac{\Delta t}{\Delta p}$ =0.05 degree/mm (determined from the results of eight distillations at different pressures); d_4^{20} 0.877; n_D^{20} 1.4756; found MR 28.37; calculated MR 28.12.

	Found %:	C 54.30; 54.39;	H 9.14; 9.05;	S 36.25; 36.30
C_4H_8S,	Calculated %:	C 54.49;	H 9.14;	S 36.37

The literature gives the following constants for ethyl vinyl sulfide: b.p. 90.5-91.5°; d_4^{14} 0.887 [3]; b.p. 91.5-92°; d_4^{15} 0.8691; n_D^{25} 1.4631 [4].

The resinous residue was steam-distilled, extracted with ether, dried, and distilled. A substance (11 g) having the following constants was obtained: b.p. 78° (5 mm); n_D^{20} 1.5114; d_4^{20} 0.9787; found MR 45.97; calculated MR 45.84.

	Found %:	C 48.10; 48.18;	H 9.40; 9.43;	S 42.17; 42.11
$C_6H_{14}S_2$.	Calculated %:	C 47.95;	H 9.39;	S 42.66

When oxidized in acetone solution with potassium permanganate, this disulfide gave a disulfone, m.p. 137°. Treatment with an aqueous solution of $PdCl_2$ gave a complex salt, m.p. 179-180°. When treated with mercuric chloride in alcohol, a yellow coloration was obtained with Methyl orange.

The disulfide isolated has, therefore, the structure of 1,2-bis(ethylthio)ethane, for which the literature gives: b.p. 210-213° at atmospheric pressure, $d_4^{15.5}$ 0.9871 [15]; m.p. of sulfone 137° [16]; m.p. of complex salt with $PdCl_2$ 179-190° [17]. The isomeric diethyl mercaptal $CH_3CH(SC_2H_5)_2$ gives a sulfone of m.p. 75° [18], and should give an acid reaction with Methyl orange in presence of excess of mercuric chloride [9].

We have obtained also previously undescribed complex salts of 1,2-bis(ethylthio)ethane with one and three molecules of mercuric chloride. 1,2-Bis(ethylthio)ethane (0.47 g) was mixed with 4.5 ml of a 20% alcoholic solution of mercuric chloride. The resulting precipitate, after recrystallization from alcohol and vacuum drying, melting at 99.5-100°.

	Found %:	Cl 17.18; 17.14;	S 15.27; 15.32	
$C_6H_{14}S_2HgCl_2$.	Calculated %:	Cl 16.81;	S 15.20	

The salt obtained as above (2 g) was shaken mechanically for 60 hours with an alcoholic solution of mercuric chloride (1.5 g of $HgCl_2$ in 10 ml of ethanol). The precipitate, after recrystallization from alcohol and vacuum drying, was obtained in the form of needles, m.p. 162°.

	Found %:	C 7.35; 7.44;	H 1.58; 1.58;	S 6.82; 6.71;	Cl 22.3; 22.1
$C_6H_{14}S_2 \cdot 3HgCl_2$.	Calculated %:	C 7.46;	H 1.46;	S 6.64;	Cl 22.03

II. Reaction of Ethyl Vinyl Sulfide with Ethanethiol

All experiments were carried out with an excess of about one molecular proportion of ethanethiol, and both the thiol and the ethyl vinyl sulfide were freshly distilled for use.

a) Addition of C_2H_5SH to $C_2H_5SCH=CH_2$ in presence of air. To 3.6 g of ethyl vinyl sulfide, contained in a flask fitted with a stirrer and cooled with ice water, 4.2 g of ethanethiol was added, and the mixture was set aside overnight. The excess of thiol was distilled off, and 5.3 g (88.3%) of 1,2-bis(ethylthio)ethane then came over at 94-95° (7 mm); it had n_D^{20} 1.5110. The product did not give an acid reaction with Methyl orange after addition of excess of mercuric chloride. The addition of ethanethiol to ethyl vinyl sulfide was entirely in the direction contrary to Markovnikov's rule.

b) Addition of C_2H_5SH to $CH_2=CHSC_2H_5$ in a vacuum in presence of traces of oxygen. The experiment was carried out in the three-ampoule apparatus described in a previous communication [9]. Ethyl vinyl sulfide (6 g) was introduced into an ampoule having a side tube, and ethanethiol (8.6 g) was introduced into another, similar ampoule. These substances were then vacuum-distilled into the third ampoule, which had a capillary neck and was cooled with liquid nitrogen. The whole system was evacuated, and the ampoule was sealed off. It was then heated at 60-70° for 25 hours, with some interruptions. Fractionation yielded 3.5 g of the thiol (in the trap) and 9.3 g (93%) of 1,2-bis(ethylthio)ethane, b.p. 61° (2.8 mm), n_D^{20} 1.5112. In presence of traces of oxygen, the addition of ethanethiol to ethyl vinyl sulfide was again in the direction contrary to Markovnikov's rule.

c) Addition of C_2H_5SH to $CH_2=CHSC_2H_5$ in presence of hydroquinone. The experiment was carried out as described above, with the exception that 0.75 g (5 mole-%) of hydroquinone was introduced into the ampoule having the capillary neck. The ethyl vinyl sulfide (6 g) and ethanethiol (8 g) were distilled before the experiment in a current of dry nitrogen. After the ampoule had been heated at 60-70° for 25 hours with some interruptions, the reaction mixture was fractionated. At room temperature and at a residual pressure of 6 mm, 10 g of substance came over directly from the ampoule and was collected in a trap; fractionation of this under atmospheric pressure yielded 5.5 g of unchanged thiol and 2.5 g of ethyl vinyl sulfide. The residue was washed from the ampoule with ether, and the ether extract was washed with alkali to remove hydroquinone, dried over calcined Na_2SO_4, and distilled, when 2.2 g of a substance of b.p. 72-80° (10 mm) and n_D^{20} 1.5056 was obtained. After redistillation the constants of the product were b.p. 72-74° (10 mm); n_D^{20} 1.5025; d_4^{20} 0.9706; found MR 45.74; calculated MR 45.84.

All of these constants, and also the formation of a sulfone of m.p. 75° by permanganate oxidation, indicate that this substance was the diethyl mercaptal $CH_3-CH(SC_2H_5)_2$. Values found for the mercaptal content were 99.8%, 100.7%, determined by titration after addition of excess of mercuric chloride in ethanol, when reaction occurs according to the equation:

$$CH_3CH(SC_2H_5)_2 + 2HgCl_2 + 2C_2H_5OH \rightarrow 2C_2H_5SHgCl + 2HCl + CH_3CH(OC_2H_5)_2. \qquad (9)$$

The yield of the mercaptal was 36.6%. The somewhat high refractive index and the extended boiling range during the first fractionation indicate the possible presence of 1,2-bis(ethylthio)ethane as impurity. The presence of hydroquinone retarded the reaction of addition contrary to Markovnikov's rule and made it possible for reaction in accordance with this rule to occur.

d) Addition of C_2H_5SH to $CH_2=CHSC_2H_5$ in presence of SO_2. The thiol (4.0 g) was cooled in an ampoule with a mixture of dry ice and acetone, 0.2 g of SO_2 was condensed in the ampoule, and then 5.3 g of cooled ethyl vinyl sulfide was added. The ampoule was transferred to a Dewar vessel containing liquid nitrogen, evacuated, and sealed off. After four days the ampoule was opened, and the mixture was fractionated, yielding:

Fraction I, b.p. 66-70° (10 mm); 5.5 g; n_D^{20} 1.5055

Fraction II, b.p. 70-80° (10 mm); 2.0 g; n_D^{20} 1.5100

Resinous residue, 1 g

After refractionation, Fraction I was titrated for mercaptal and gave values of 91.4%, 91.9%; the yield of this product was 51%. Fraction II corresponded in its boiling point and refractive index to the isomeric 1,2-bis(ethylthio)-ethane. In the presence of SO_2 addition occurred mainly in accordance with Markovnikov's rule.

III. Reaction of H_2S with $CH_2=CHSC_2H_5$

Ethyl vinyl sulfide (8.9 g) was introduced into an ampoule, into which 5.6 g (1.5 moles per mole of ethyl vinyl sulfide) of hydrogen sulfide was then condensed. The cooled ampoule was evacuated and sealed off. After

2.5 months the ampoule was opened, the excess of hydrogen sulfide was evaporated off, and the mixture was fractionated, yielding:

Fraction I, b.p. 60° (9 mm); 7.1 g

Fraction II, b.p. 161° (9 mm); 4.2 g

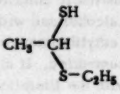
Fraction I was 2-ethylthioethanethiol $C_2H_5SCH_2CH_2SH$, obtained in 58.6% yield.

After refractionation this substance had b.p. 60° (9 mm); n_D^{20} 1.5273; d_4^{20} 1.0337; found MR 36.47; calculated MR 36.53.

	Found %:	C 39.67; 39.62;	H 8.33; 8.36;	S 52.05; 52.09
$C_4H_{10}S_2$.	Calculated %:	C 39.30;	H 8.24;	S 52.46

For this substance the literature [19] gives b.p. 188° at atmospheric pressure.

This thiol was stable and was not decomposed by strong hydrochloric acid; the isomeric 1-ethylthioethanethiol



should be decomposed by acid with formation of "trithioacetaldehyde" (2,4,6-trimethyl-s-trithiane), like the previously described 1-alkoxyethanethiols [20].

Fraction II gave no acid reaction with Methyl orange when mixed with excess of mercuric chloride. It was bis(2-ethylthioethyl) sulfide obtained in 40.3% yield. At room temperature it solidified to a crystalline mass. It had n_D^{20} 1.5460; d_4^{20} 1.0542; found MR 63.21; calculated MR 63.04.

	Found %:	C 45.97; 45.92;	H 8.74; 8.66;	S 45.74; 45.35
$C_8H_{18}S_3$.	Calculated %:	C 45.66;	H 8.62;	S 45.72

According to the literature [20], this trisulfide has b.p. 173-175° (21 mm) and m.p. 17°.

In presence of traces of oxygen, hydrogen sulfide adds to ethyl vinyl sulfide entirely in the direction contrary to Markovnikov's rule.

IV. Polymerization of Ethyl Vinyl Sulfide

a) Polymerization of ethyl vinyl sulfide in presence of $FeCl_3$ and $SnCl_2$. The results of this series of experiments are given in Table 2.

TABLE 2

Polymerization of Ethyl Vinyl Sulfide in Presence of $FeCl_3$ and $SnCl_2$. Amount of ethyl vinyl sulfide taken: 2.65 g, i.e., 3 ml

Expt. No.	Catalyst as alcoholic solution (drops)		Yield of resinous residue (g)	Amount of unchanged monomer (g)
	1% $SnCl_2$	5% $FeCl_3$		
1	2	–	0.1	2.3
2	4	–	0.1	2.3
3	–	1	0.1	2.4
4	–	2	0.1	2.2
5	–	3	0.3	2.2
6	–	–	0.1	2.3

The polymerization was carried out in sealed tubes heated, with some interruptions, for 54 hours at 50°. It will be clear from the results in Table 2, that under these conditions, $SnCl_2$ and $FeCl_3$ do not promote the polymerization of ethyl vinyl sulfide. Addition of catalyst to the boiling substance does not increase the yield of polymer, whereas, under these conditions, ethyl vinyl ether gives high yields of highly viscous polymers [11, 12].

b) Polymerization of ethyl vinyl sulfide in presence of sunlight. A sealed glass tube containing 2.5 g of ethyl vinyl sulfide was exposed to sunlight. By the tenth day the liquid had acquired the consistency of glycerol. After 2.5 months, fractionation in a current of dry nitrogen yielded 0.8 g of monomer (n_D^{20} 1.4768). The polymer was freed from monomer in a vacuum desiccator, at first at room temperature, and then at 40-45°. The yield of polymer was 1.5 g (60%). The polymer was found to be soluble in the cold in dioxane, dichlorethane, and ether, but insoluble in ethanol. It was not found possible to determine the molecular weight by the cryoscopic method owing to the very small depression; the molecular weight was, therefore, higher than 5000.

Found %: C 54.58; 54.53; H 9.21; 9.17; S 36.09; 36.33

$(C_4H_8S)_p$. Calculated %: C 54.49; H 9.14; S 36.37

c) Polymerization of ethyl vinyl sulfide in presence of 2,2'-azobis(2-methylpropionitrile). A mixture of 5 g of ethyl vinyl sulfide and 0.01 g (0.2% by weight) of 2,2'-azobis(2-methylpropionitrile) was heated continuously for 80 hours in a sealed tube in a thermostat at 60°. The contents of the tube were then dissolved in 10 ml of dry benzene, and the solution was poured slowly into 200 ml of dry methanol. The reprecipitation was repeated twice, and the yield of polymer was then 2.5 g (50% on the amount of ethyl vinyl sulfide taken). The amount of unchanged monomer, determined in the methanol solutions from the reprecipitations (addition of excess of mercuric chloride and titration with 0.1 N NaOH) was 2.45. The polymer was dried at 60° in a vacuum to constant weight.

Found %: C 54.86; 55.01; H 9.14; 9.03; S 36.27; 36.27

$(C_4H_8S)_p$. Calculated %: C 54.49; H 9.14; S 36.37

V. Reaction of Ethyl Vinyl Sulfide with Mercuric Chloride

a) Reaction of ethyl vinyl sulfide with an alcoholic solution of mercuric chloride. Ethyl vinyl sulfide (0.13 g) was treated with 4.5 ml of a 20% solution of mercuric chloride in ethanol, and the mixture was set aside overnight. The precipitate was filtered off, washed with alcohol and with ether, and vacuum-dried to constant weight. The yield of precipitate was 0.37 g (96.2%). The ethylthiomercury chloride was recrystallized from boiling xylene, washed with alcohol and with ether, and vacuum-dried. It did not melt when heated to 200°, but it slowly decomposed at about 300-350°, which is in accord with the literature [21].

Found %: S 10.78; 10.73

C_2H_5SHgCl. Calculated %: S 10.79

It has been shown above that, when the sulfide is treated with a 20% solution of mercuric chloride in ethanol, the formation of hydrogen chloride is also quantitative in accordance with Equation 6; subsequent titration with 0.1 N NaOH provides a method for the quantitative analysis of the sulfide.

b) Reaction of ethyl vinyl sulfide with an aqueous solution of mercuric chloride. Ethyl vinyl sulfide (1.1 g) was introduced into 75 ml of an aqueous solution of mercuric chloride (4.1 g of $HgCl_2$ in 75 ml of water). On the next day the reaction mixture was transferred to a flask and fractionated in a continuous current of dry nitrogen. The aqueous part was collected in receivers, and the vapor was passed on through a trap containing alcohol and cooled with snow and salt. The contents of the trap had a strong odor of acetaldehyde and gave a magenta color with Schiff's reagent; the aqueous distillate was acid to Methyl orange. The precipitate weighted 3.13 g (87% yield). It was treated as in the previous experiment, and it did not melt below 200°, i.e., it had the properties of ethylthiomercury chloride.

TABLE 3

Decomposition of the Complex with Water and with Alcohol

Expt. No.	Amount of sulfide (g)	Amount of $HgCl_2$ (g) in 50 ml ether	Yield of pink complex salt (g)	Ppt. treated with	Yield of ethylthiomercury chloride (%)
1	1.15	4	5.4	H_2O	23
2	1.05	4	5.2	C_2H_5OH	21

c) Reaction of ethyl vinyl sulfide with an ethereal solution of mercuric chloride. Ethyl vinyl sulfide (70.1 g) was mixed with 25 ml of an ethereal solution of mercuric chloride (1 g of mercuric chloride in 25 ml of absolute ether). After a time a pink precipitate formed, and, when the ether was removed, this began to change rapidly in color, through lilac to black. The precipitate melted at 32-34°, sintering into a black lump.

Found %: C 10.15; 10.21; H 1.97; 1.84; S 8.05; 7.86

$C_{12}H_{24}S_3 \cdot 4HgCl_2$. Calculated %: C 10.55; H 1.76; S 7.04

This composition corresponds approximately to the formula

$$4HgCl_2 \cdot 3C_2H_5-SCH=CH_2.$$

This complex salt of ethyl vinyl sulfide with mercuric chloride was unstable, and it decomposed readily when treated with alcohol or water. The aqueous or alcoholic solution then acquired an aldehyde reaction and acidity, and the pink complex salt was converted into a white infusible precipitate of ethylthiomercury chloride (Table 3); this conversion was not, however, quantitative.

SUMMARY

1. Conditions have been found for the synthesis of ethyl vinyl sulfide in 60% yield.

2. It has been shown that ethanethiol and hydrogen sulfide add to ethyl vinyl sulfide, in the air and in presence of traces of oxygen, in the direction contrary to that required by Markovnikov's rule; but, in presence of hydroquinone or of the acid catalyst SO_2, addition of the thiol proceeds in accordance with the rule.

3. It has been shown that polymerization of ethyl vinyl sulfide does not occur in presence of the ionic catalysts $FeCl_3$ and $SnCl_2$, but occurs in presence of 2,2'-azobis(2-methylpropionitrile), under the action of sunlight, and when kept for a long time.

4. The reaction of ethyl vinyl sulfide with mercuric chloride in alcoholic and aqueous solutions leads to the formation of a mercurated salt of ethanethiol, but in ethereal solution the product is an unstable complex salt, which is decomposed by water and alcohol.

5. It has been shown that ethyl vinyl sulfide, although the sulfur analog of ethyl vinyl ether, has a considerably greater tendency to undergo addition reactions that are contrary to Markovnikov's rule and have a free-radical character.

Received February 10, 1953

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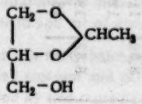
REACTIONS BETWEEN VINYL COMPOUNDS AND MULTIFUNCTIONAL COMPOUNDS

COMMUNICATION 2. REACTIONS OF VINYL ETHERS WITH POLYVINYL ALCOHOL

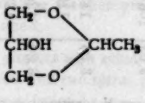
M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya

In our communication [1] relating to the reactions of alkyl vinyl ethers (ethyl vinyl and butyl vinyl) with glycerol, it is shown that the mobile hydrogens of the free hydroxyl eliminate alkoxyl groups from the partial mixed acetals with formation of cyclic acetals of glycerol. As a result of these transformations, the following acetals were obtained:



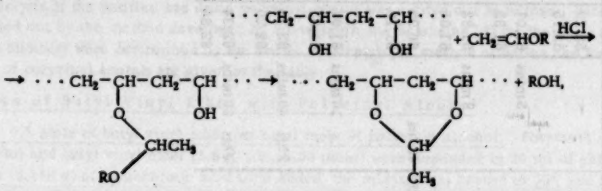
(I)

and



(II)

In connection with the discovery of this method of synthesizing cyclic acetals, it was considered to be of interest to study the reaction of vinyl ethers with polyhydric alcohols, such as polyvinyl or polyallyl alcohols, which have much higher numbers of hydroxyl groups in their molecules than glycol or glycerol. In this case the reaction may be represented as follows:



(III)

(R is alkyl or aryl).

In the literature there is only an indication of the possibility of the reaction of polyvinyl alcohol with the lower alkyl vinyl ethers [2].

Our investigations have established that, when alkyl and aryl vinyl ethers react with polyvinyl alcohol, a polyacetal of polyvinyl alcohol (III) and the corresponding monohydric alcohol are formed, i.e., the reaction proceeds analogously to the synthesis of acetals from glycerol. The formation of polyacetals of polyvinyl alcohol by reaction of the latter with vinyl ethers evidently also passes through a mixed partial acetal, which, being unstable, reacts with formation of cyclic polyacetals and separation of a monohydric alcohol. When there is excess of vinyl ether, the alcohol or phenol that separates reacts with this excess and forms the corresponding acetal. These ideas are confirmed, first by the fact that in the course of the syntheses of polyacetals no appreciable amounts of acetaldehyde were detected, and second by the high yields of acetals.

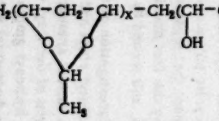
In the investigation of the reaction between polyvinyl alcohol and vinyl ethers, the examples of the latter selected were butyl vinyl and phenyl vinyl ethers, and the ratio of components was varied and various catalysts were taken in various amounts, with the object of ensuring that the conditions were such as to exclude the possibility of the hydrolysis of the vinyl ether. Analysis of the resulting polyacetals of polyvinyl alcohol showed that the replacement of hydroxyl groups of the polyalcohol proceeded almost to completion under various conditions, attaining 95-97% of the theoretical value.

The observed discrepancies between the determined and calculated values in the elementary composition of the polyacetals, which were somewhat higher than those normally accepted for pure individual compounds, must be explained on the basis of the nature of highly polymeric substances.

Analysis of Polyacetals Obtained by the Reaction of Vinyl Ethers with Polyvinyl Alcohol

Components, and their amounts			Experimental conditions			Elementary composition				Chemical composition			Rel. viscosity of 1% soln. in dichloroethane	Yield of polyacetal (% of theoretical)
						found		calculated						
Polyvinyl alcohol (basal moles)	Butyl vinyl ether (moles)	Phenyl vinyl ether (moles)	Amount of catalyst (g)	Temp. (°C)	Time	%C	%H	%C	%H	Hydroxyl No.	OH groups (%)	Acetal groups (%)		
+	–	–	–	–	–	53.29 53.15	9.22 9.02	54.54	9.09	1064.0	32.3	–	–	–
1	0.5	–	0.146 HCl	50	5 mins	61.07 61.35	8.74 8.92	62.32•	8.36	113.58 116.40	3.40 3.54	43.77 44.42	3.67	93.0
1	1	–	0.292 HCl	50	8 mins	61.83 61.65	8.73 8.97	62.29	8.80	120.0 120.0	3.65 3.65	44.20 44.41	3.70	92.0
1	0.5	–	0.042 HCl	18-20	48 hrs	60.92 61.10	8.88 9.11	62.42	8.79	95.10 99.80	2.88 3.03	43.39 43.12	3.71	91.0
1	1	–	0.131 H_3PO_4	50	10 mins	61.07 61.33	9.31 9.14	61.83	8.82	188.0	5.73	43.35	4.56	86.2
1	–	0.5	0.218 HCl	50	2 hrs 40 mins	62.35 62.20	9.01 9.09	62.29	8.80	115.90 120.40	3.54 3.65	43.76 43.29	3.87	98.7
1	–	1	0.146 HCl	50	2 hrs 50 mins	62.34 62.34	9.00 8.99	61.80	8.82	196.20 185.30	5.95 5.64	42.38 42.41	6.31	90.7

• . . . $CH_2(CH-CH_2-CH)_x-CH_2(CH-CH_2)_y$ . . .



EXPERIMENTAL

The sample of polyvinyl alcohol used in this work had the following characteristics: content of acetate groups 1.82%; acid number 1.1; content of volatile substances, determined by drying to constant weight over calcium chloride, 3.31%; specific viscosity of a 1% aqueous solution, determined in an Ostwald viscosimeter, 1.93. The polyvinyl alcohol was brought to a highly dispersed condition by grinding in a ball mill and passage through a sieve having 10,000 mesh per sq.cm.

The vinyl ethers had the following constants: butyl vinyl ether, b.p. 93-94°, n_D^{20} 1.4030; phenyl vinyl ether, b.p. 46-47° (11-12 mm); n_D^{20} 1.5228.

Procedure

The synthesis was carried out in a three-necked flask fitted with stirrer, mercury seal, thermometer, and reflux condenser attached to a spiral receiver cooled to −40 to −60°. The polyvinyl alcohol and vinyl ether were suspended in chloroform. After 30 minutes the catalyst (hydrochloric acid) was added, and the reaction was carried out at room temperature or at 50°. When reaction was complete, as indicated by the formation of a homogeneous clear solution, the reaction mixture was neutralized with ammonia. The reaction product was precipitated with ether, and was then washed with 150 ml of distilled water and air-dried.

When butyl vinyl ether was used, before precipitation of the product with ether the bulk of the volatile part was distilled off under reduced pressure and collected in the receivers and two spiral traps cooled to −40 to −60°. The dried product was purified by two reprecipitations from acetone solution by means of distilled water, and it was then dried to constant weight over calcium chloride and subjected to analysis. Half of the diethyl ether from the precipitation was distilled, to separate volatile reaction products, and the other half was transferred to a weighed porcelain dish and evaporated in the air. The wash water, and also the aqueous acetone solutions from the reprecipitation of the polyvinyl acetals were also evaporated in the air. The products so isolated were taken into account in the general balance sheet of the reaction.

Analysis of the purified and dried polyvinyl acetal was carried out as follows: determination of acetal groups was carried out by the method developed by Soloveichik and Balandina [3] for the analysis of polyvinylbutyral. The hydroxyl numbers were determined by the acetic acid–pyridine method of Barley and Belsing [4]. The results of the analyses of polyvinyl acetals are given in the table.

Reaction of Butyl Vinyl Ether with Polyvinyl Alcohol

a) 0.5 Mole of butyl vinyl ether per basal mole of polyvinyl alcohol. Polyvinyl alcohol (4.4 g, i.e., 0.1 basal mole) and butyl vinyl ether (5.0 g, i.e., 0.05 mole) were suspended in 30 ml of chloroform. After 30 minutes, ten drops (0.146 g) of hydrochloric acid were added, the mixture was heated to 50°, and reaction was complete in five minutes. The yield of purified polyacetal was 5.3 g (93%). From the ether solution, 1.08 g (29.2%) of butyl alcohol was isolated (this contained chloroform impurity that was difficult to remove). The boiling point of the butyl alcohol was 113-114°, and the value of n_D^{20} was 1.4032; it reacted vigorously with sodium and gave the characteristic color for alcohols in Agulhon's reaction [5], but it also gave a positive Beilstein test for chlorine.

b) One mole of butyl vinyl ether per basal mole of polyvinyl alcohol. Polyvinyl alcohol (4.4 g, i.e., 0.1 basal mole) and butyl vinyl ether (10 g, i.e., 0.1 mole) were suspended in 30 ml of chloroform. After 30 minutes, 20 drops (0.292 g HCl) of hydrochloric acid were added, and five minutes later the temperature of the reaction mixture had risen from 50° to 58°. Reaction was complete eight minutes after the addition of catalyst. After the purification treatment, 5.23 g (92%) of the polyacetal was obtained. Distillation of the ether solution yielded:

Fraction I, b.p. 38-41° (15 mm); 2.15 g; n_D^{20} 1.4045

Fraction II, b.p. 74-78° (15 mm); 2.71 g; n_D^{20} 1.4115

Redistillation of Fraction I yielded a substance of b.p. 113-114°, n_D^{20} 1.4028, having the characteristic odor of butyl alcohol and reacting vigorously with sodium.

Two redistillations of Fraction II yielded a substance having b.p. 77-80° (15 mm), d_4^{20} 0.8319 and n_D^{20} 1.4118. Its constants differed somewhat from those given in the literature for the dibutyl acetal: b.p. 184-185°; d_4^{20} 0.8267; n_D^{20} 1.4090 [6]; this, as already indicated above, is explained by the presence of chloroform impurity, which we did not succeed in separating.

Found %: C 68.50; 68.40; H 12.57; 12.60

$C_{10}H_{22}O_2$. Calculated %: C 68.97; H 12.65

c) Experiment in presence of traces of catalyst (hydrochloric acid). The experiments described, in which 0.5 mole or one mole of butyl vinyl ether reacted with one basal mole of polyvinyl alcohol, were performed in presence of a comparatively large amount of aqueous hydrochloric acid and at an elevated temperature, and these conditions could themselves lead to hydrolysis of the vinyl ether. At the same time, therefore, experiments were carried out with a very small amount of hydrochloric acid. The quantities of the original components were kept the same, but the experiments were carried out in presence of three drops of hydrochloric acid (0.042 g) and at room temperature. Under these conditions, and with 0.5 mole of butyl vinyl ether per basal mole of polyvinyl alcohol, reaction was complete in 48 hours. After treatment of the resulting solution according to the procedure described above, 5.23 g (91%) of purified polyacetal and 0.89 g (24%) of butyl alcohol (b.p. 113-114°, n_D^{20} 1.3982) were obtained.

d) Experiment in presence of phosphoric acid (as catalyst). In order to exclude the effect of water on the reaction between polyvinyl alcohol and vinyl ethers, an experiment was carried out in presence of anhydrous phosphoric acid (five drops, 0.1315 g) at 50°. Reaction was complete in ten minutes with rise in the temperature of the mixture to 61.5°. The amounts taken for reaction were 4.4 g of polyvinyl alcohol and 10 g (0.1 mole) of butyl vinyl ether, and the products isolated were 4.95 g (86.2%) of purified polyacetal and 5.65 g (65%) of acetaldehyde dibutyl acetal, b.p. 77-80° (15 mm); n_D^{24} 1.4096; n_D^{20} 1.4120.

Analysis of Acetaldehyde Dibutyl Acetal

Found %: C 68.33; 68.28; H 12.66; 12.57

$C_{10}H_{22}O_2$. Calculated %: C 68.97; H 12.65

Reaction of Phenyl Vinyl Ether with Polyvinyl Alcohol

a) 0.5 Mole of phenyl vinyl ether per basal mole of polyvinyl alcohol. Polyvinyl alcohol (6.6 g) and phenyl vinyl ether (9.0 g, i.e., 0.075 mole) were suspended in 45 ml of chloroform. After thirty minutes, 15 drops of hydrochloric acid (0.218 g) were added and the mixture was heated to 50°, and after a further 2 hours 40 minutes, reaction was complete, the temperature having risen to 58°. The yield of purified polyacetal was 8.34 g (98.7%).

The ether solution was divided into two parts, transferred to two porcelain dishes, and exposed to air for evaporation of solvent. In the first dish, after the evaporation there remained 3.45 g (49.3% of the calculated amount) of colored syrupy material, having n_D^{20} 1.5412 and giving a characteristic color for phenol with ferric chloride. The residue in the second dish was used for the steam distillation of phenol. For the quantitative determination of the phenol isolated, Koppeschaar's method was used [7], the amount found being 1.752 g.

b). One mole of phenyl vinyl ether per basal mole of polyvinyl alcohol. A mixture of 4.4 g (0.1 basal mole) of polyvinyl alcohol and 12.0 g (0.1 mole) of phenyl vinyl ether was suspended in 30 ml of chloroform. After 30 minutes, ten drops of hydrochloric acid (0.146 g) were added and the mixture was heated to 50°. Reaction was complete in 2 hours 50 minutes. The yield of purified polyacetal was 5.17 g (90.7%).

After removal of ether by evaporation, the residue was 8.65 g of a colored syrupy material having n_D^{20} 1.5522. After repeated vacuum distillation this yielded 1.98 g (18.5% of the calculated amount) of a substance, b.p. 169° (28 mm) and n_D^{20} 1.5565, corresponding to acetaldehyde diphenyl acetal, and also 0.21 g of crystalline phenol.

Analysis of Acetaldehyde Diphenyl Acetal

Found %: C 77.97; 78.02; H 6.79; 6.81

$C_{14}H_{14}O_2$. Calculated %: C 78.51; H 6.54

SUMMARY

1. A study has been made of the reactions between polyvinyl alcohol and butyl vinyl and phenyl vinyl ethers, the proportions of components being varied.

2. It has been shown that reaction between polyvinyl alcohol and butyl vinyl or phenyl vinyl ether leads to the formation of polyacetals of polyvinyl alcohol.

3. It is possible that the formation of the polyacetals of polyvinyl alcohol passes through the stage of mixed acetals, which subsequently undergo cyclization.

Received March 25, 1953

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 61. DECARBOXYLATION OF DICARBOXYLIC ACIDS DURING POLYCONDENSATION

V. V. Korshak and S. V. Rogozhin

The decomposition of adipic acid with evolution of carbon dioxide in the course of the polycondensation of the acid with 1,6-hexanediamine was first discovered by one of us in collaboration with Zamyatina [1]. It was shown that the decomposition of the acid was of great significance in the polycondensation reaction, and this induced us to make a more detailed study of this reaction for various dicarboxylic acids under polycondensation conditions.

In a systematic study of the decarboxylation of dicarboxylic acids by heat, we examined oxalic, malonic, succinic, glutaric, adipic, pimelic, azelaic, and sebacic acids [2, 3]. It was found that the thermal decomposition of dicarboxylic acids resulted in the formation of carbon dioxide, monocarboxylic acids, sometimes cyclic ketones, and other products. The formation of a monocarboxylic acid may be represented by the following equation:

$$HOOC(CH_2)_n\,COOH \rightarrow CH_3(CH_2)_{n-1}\cdot COOH + CO_2.$$

With increase in the length of the carbon chain of the acid its stability to the action of high temperature increases and its decarboxylation temperature rises correspondingly from 140° for malonic acid to 350° for sebacic acid. It was noted that acids having an even number of carbon atoms decompose at a higher temperature than acids having an odd number of carbon atoms (the number of carbons in the chain being greater than one). The results obtained pointed to the conclusion that, in the polycondensation of dicarboxylic acids, the temperature conditions must be such as to obviate decomposition of the acid. The conversion of dicarboxylic acids into monocarboxylic acids or cyclic ketones as a result of decarboxylation affects the proportions of starting substances, which results in reduction in the molecular weight of the polymers formed, as was shown by one of us with Rafikov [4], with Golubev [5], with Kolesnikov [6], and with others, the cause of this being the premature termination of the chain [7, 8].

The object of the present investigation was to determine the effect on the decomposition of dicarboxylic acids of exposure to the conditions of polycondensation with other bifunctional compounds. The presence of a second compound, and also reaction with this formation of macromolecular compounds, is bound to have an effect on the behavior of the dicarboxylic acids. It was of great interest also to study the effect of the decarboxylation of the acids on the process of macromolecule formation. In order to obtain an answer to these questions we have studied the decomposition of oxalic, malonic, succinic, adipic, and sebacic acids under the conditions of their polycondensation with ethylene glycol.

EXPERIMENTAL

The rate of the decomposition of the dicarboxylic acid was determined from the amount of the resulting carbon dioxide, which was absorbed either in standard alkali or in U-tubes filled with soda asbestos, the amount evolved then being determined by the increase in weight. The polycondensation reaction was carried out in a current of dry nitrogen, which was first purified from oxygen and carbon dioxide. A diagram of the apparatus is given in Fig. 1.

Equimolecular amounts of the acid and ethylene glycol were placed in a test tube and heated in a bath containing Wood's metal. Nitrogen, dry and purified from oxygen and carbon dioxide, was passed continuously into the tube. In the polycondensation of ethylene glycol with succinic, adipic, and sebacic acids, the duration of the reaction was in each case nine hours. During the first two hours, the nitrogen was passed through the reflux condenser 2 and the distillation condenser 3, and carried away the carbon dioxide and other volatile products. The presence of the reflux condenser enables loss, due to volatility, of the original substances to be avoided.

After two hours, when the original compounds had entered almost entirely into the reaction, the nitrogen, containing water vapor and carbon dioxide, passed only through the condenser 3, in which most of the water vapor condensed. The remaining traces of water vapor were absorbed in the Drechsel 5, containing concentrated sulfuric acid and in a U-tube containing calcined calcium chloride. After being freed from water vapor, the nitrogen and the carbon dioxide formed by the breakdown of carboxyl groups passed to the absorption system, in which the carbon dioxide was absorbed.

Experimental Results

The experiments on the polycondensation of ethylene glycol with oxalic and malonic acids were carried out at 90° and 140°. The carbon dioxide evolved was absorbed with a solution of caustic soda. The results for oxalic acid are given in Table 1, and those for malonic acid in Table 2. In these experiments no polyesters were formed, and the reaction products were, therefore, not investigated in greater detail.

TABLE 1

Decomposition of Oxalic Acid when Heated with Ethylene Glycol

No.	Duration of heating (hr)	Amount of acid decomposed (%) at					
		90°	100°	110°	120°	130°	140°
1	0.5	0.22	0.73	1.90	2.92	5.70	21.90
2	1.0	0.76	1.54	4.90	6.00	14.10	34.50
3	2.0	1.38	3.28	10.40	15.30	29.30	45.60
4	3.0	1.97	4.75	14.50	24.10	42.70	48.60
5	4.0	2.62	6.90	20.50	31.40	49.30	49.80
6	5.0	3.38	9.01	24.30	35.70	49.60	49.90
7	6.0	4.23	11.00	–	40.10	50.00	50.00

TABLE 2

Decomposition of Malonic Acid when Heated with Ethylene Glycol

No.	Duration of heating (hr)	Amount of acid decomposed (%) at				
		90°	100°	110°	120°	140°
1	0.5	1.50	3.10	5.95	16.50	27.30
2	1.0	4.20	6.40	11.90	24.40	33.60
3	2.0	6.70	13.40	20.60	30.30	37.90
4	3.0	9.40	19.30	25.80	36.40	41.40
5	3.0	12.30	22.40	28.50	38.10	43.20
6	5.0	15.60	25.50	31.60	38.10	44.90

In the case of succinic, adipic, and sebacic acids, polycondensation occurred when they were heated with ethylene glycol with formation of polyesters. The nature and number of the end groups of the polyester, and also its molecular weight, were determined for each sample for the various reaction temperatures, and they are given in tables; the results for succinic acid in Table 3, for adipic acid in Table 4, and for sebacic acid in Table 5.

TABLE 3

Polycondensation of Succinic Acid with Ethylene Glycol

Reaction temp. (°C)	Amt. of COOH groups split off (%)	Characteristics of polyester						
		ml of 0.1 N alkali consumed per g of polyester in determining		Amt. of COOH groups split off, calcd. from titration data	sp. viscosity of 0.5% solution	molecular weight		
		OH groups	COOH groups			by hydroxyl groups	by carboxyl groups	by viscosity
240	2.81	10.60	10.65	0.51	0.026	945	949	840
250	7.01	8.00	8.25	2.30	0.037	1250	1215	1190
260	14.25	6.25	4.78	20.30	0.053	1600	2095	1680
270	21.30	7.34	4.01	35.30	0.051	1360	2490	1610
280	–	13.67	3.40	68.24	0.030	734	2945	940

In the second column of Table 3 we give the amount of carboxyl groups split off as a percentage of the total amount; these figures are calculated from the amount of carbon dioxide evolved. The figures in the fifth column of Table 3 (amount of carboxyl groups eliminated from the polyester) were calculated on the basis of the results of the titration of the carboxyl end groups of the polyester, and they indicate the deficiency in the amount of carboxyl groups in comparison with the amount to be expected on the basis of the viscometric determination of molecular weight.

TABLE 4

Polycondensation of Adipic Acid with Ethylene Glycol

Reaction temp. (°C)	Amt. of COOH groups split off (%)	Characteristics of polyester: ml of 0.1 N alkali consumed per g of polyester in determining OH groups	ml of 0.1 N alkali consumed per g of polyester in determining COOH groups	Amt. of COOH groups split off, calcd. from titration data	sp. viscosity of 0.5% solution	molecular weight: by hydroxyl groups	by carboxyl groups	by viscosity
180	0.33	–	31.20	–	0.014	–	320	426
190	0.53	–	31.55	–	0.015	–	317	474
200	0.74	–	22.25	–	0.017	–	448	525
210	1.17	–	13.90	0.10	0.024	–	721	720
220	2.12	12.15	10.00	5.5	0.031	800	1000	945
230	4.75	10.00	7.55	4.20	0.042	1000	1828	1270
240	9.54	4.96	6.24	–	0.056	2020	1600	1670
250	14.65	4.74	4.28	–	0.088	2100	2350	2670
260	–	4.02	3.92	17.10	0.071	2500	2548	2140
270	20.80	6.90	2.95	40.90	0.066	1450	3390	2000
280	29.00	7.70	2.32	65.80	0.049	1300	4300	1470

TABLE 5

Polycondensation of Sebacic Acid with Ethylene Glycol

Reaction temp. (°C)	Amt. of COOH groups split off (%)	Characteristics of polyester: ml of 0.1 N alkali consumed per g of polyester in titration of COOH groups	Amt. of COOH groups split off, calcd. from titration data	sp. viscosity of 0.5% solution	molecular weight: by carboxyl groups	by viscosity
230	0.002	9.12	–	0.030	1000	1100
240	0.003	6.48	2.60	0.042	1540	1500
250	0.005	5.20	4.62	0.057	1950	1860
260	0.004	4.36	7.40	0.059	2300	2130
270	0.012	3.68	5.10	0.072	2740	2600
280	0.023	3.22	4.50	0.082	3100	2960

The amount of carboxyl groups eliminated from the polyester characterizes the extent to which the high temperature has affected its carboxyl end groups. A knowledge of this quantity permits us to estimate the difference in thermal stability of the carboxyl groups in the original acid, and of those in the polyester.

Discussion of Results

The investigation of the decomposition of dicarboxylic acids when heated in presence of glycols, i.e., under polycondensation conditions, shows that in the free condition dicarboxylic acids decompose considerably more slowly than under polycondensation conditions. For example, we have previously established that no appreciable decomposition occurs below 110° for oxalic alone, and below 240° for adipic acid alone [3, 4]. When, however, oxalic acid is heated with ethylene glycol for five hours at 110°, about 25% of the acid is decomposed. In the same way, when adipic acid is heated with ethylene glycol, evolution of carbon dioxide is observed already at 150°.

The decomposition of oxalic acid during its reaction with ethylene glycol becomes detectable already at 90°, and it increases greatly with rise of temperature, as can be seen from Fig. 2, in which graphs are shown for the decomposition of oxalic acid at various temperatures. The decomposition of malonic acid at 90° is still more vigorous than that of oxalic acid. It increases with rise in temperature, but not as rapidly as that of oxalic acid, as can be seen clearly from Fig. 3, in which graphs are shown for the decomposition of malonic acid at various temperatures.

In the study of the reactions of ethylene glycol with oxalic and malonic acids under the conditions described, in no case was the formation of macromolecular polyesters observed: the reaction mixture finally obtained contained only the original substances, their decomposition products, and substances formed by the interaction of substances contained in the mixture . Hence, the very low thermal stability of oxalic and malonic acids may be regarded as the main cause of their inability to form polyesters by reaction with ethylene glycol. As a result of the elimination of carboxyl groups, oxalic and malonic acids are converted into formic and acetic acids respectively, and these can give only esters of low molecular weight by reaction with glycols.

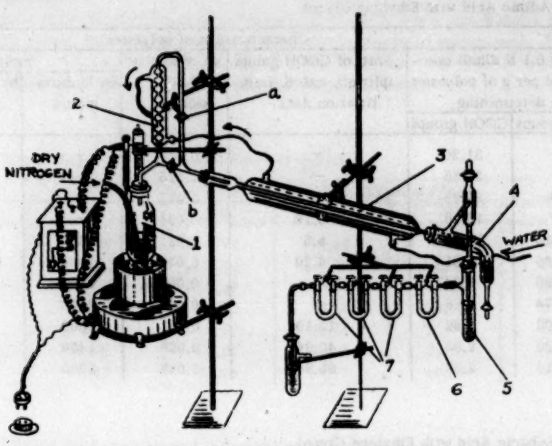

Fig. 1. Diagram of apparatus for the polycondensation of dicarboxylic acids with glycols: 1) condensation tube; 2) reflux condenser; 3) distillation condenser; 4) receiver for reaction water; 5) Drechsel bottle containing concentrated sulfuric acid; 6) calcium chloride U-tube; 7) soda asbestos absorption tubes.

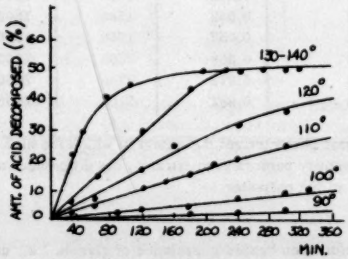

Fig. 2. Decomposition of oxalic acid during polycondensation with ethylene glycol.

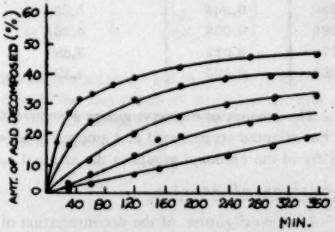

Fig. 3. Decomposition of malonic acid during polycondensation with ethylene glycol.

Succinic, adipic, and sebacic acids are distinguished by considerably higher thermal stabilities, and, when heated with ethylene glycol, macromolecular polyesters are generally formed. The study of the decomposition of these acids was carried out at higher temperatures.

When succinic acid was heated with ethylene glycol, appreciable decomposition of the acid was observed from 240° upward. Fig. 4 shows the increase in the amount of carboxyl groups eliminated with rise in temperature and the variation in the molecular weight of the polyester formed. It is quite obvious in this case that the molecular weight, as determined by carboxyl groups, increases, whereas the molecular weight values determined from viscosity in solution and by hydroxyl groups rises to a maximum and then falls. The explanation of this is that, as a result of decarboxylation, the number of carboxyl groups in the polymer falls, leading to an apparent increase in molecular weight, whereas in actual fact the molecular weight falls, as is shown by viscosity measurements on solutions of the polyester.

In the case of the polycondensation of ethylene glycol with adipic acid, appreciable decomposition of the latter begins at 250°, and it is again manifested by a fall in the molecular weight of the resulting polyester, as determined by viscosity and hydroxyl groups. In contrast to this, the molecular weight determined by carboxyl groups, as in the case of succinic acid, continues to rise, and this is to be explained in the same way as before.

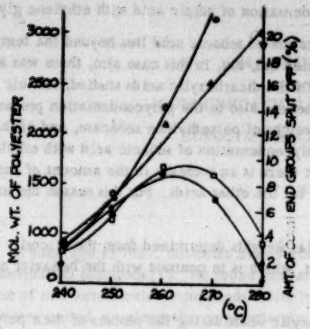

Fig. 4. Variation in the molecular weight of polyethylene succinate, and of the amount of carboxyl groups eliminated, with the temperature of the polycondensation of succinic acid with ethylene glycol: □ = molecular weight determined from the viscosity of a solution of the polyester; ● = molecular weight determined by hydroxyl groups; Δ = molecular weight determined by carboxyl groups; o = amount of carboxyl groups split off.

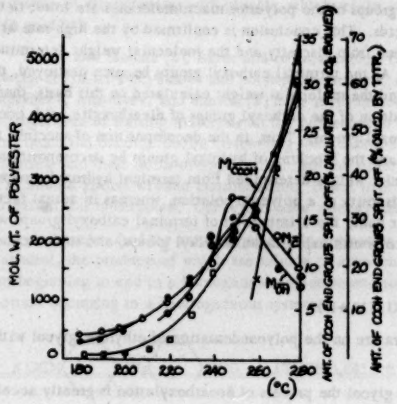
MOL. WT. OF POLYESTER
ANT. OF COOH END GROUPS SPLIT OFF (% CALCULATED FROM CO2 EVOLVED)
ANT. OF COOH END GROUPS SPLIT OFF (% CALCD. BY TITR.)
(°C)

Fig. 5. Variation in the molecular weight of polyethylene adipate, and of the amount of carboxyl groups eliminated, with the temperature of the polycondensation of adipic acid with ethylene glycol: o = molecular weight determined from the viscosity of a polyester solution; ● = molecular weight determined by hydroxyl groups; o = molecular weight determined by carboxyl groups; □ = amount of carboxyl groups split off, calculated from amount of CO_2 evolved; x = amount of carboxyl groups split off, calculated from titration data.

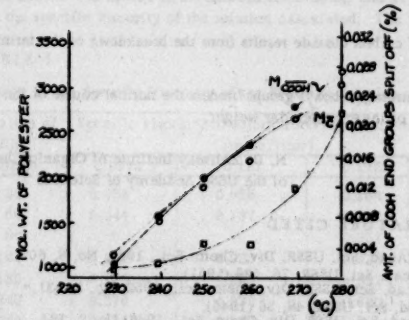

Fig. 6. Variation in the molecular weight of polyethylene sebacate, and of the amount of carboxyl groups eliminated, with the temperature of the polycondensation of sebacic acid with ethylene glycol: o = molecular weight determined from the viscosity of a polyester solution; ● = molecular weight determined by carboxyl groups; □ = amount of carboxyl groups split off.

Fig. 5 shows the variation of the molecular weight of polyethylene adipate, and of the amount of carboxyl groups eliminated, with change in the temperature of the polycondensation of adipic acid with ethylene glycol.

As we have shown previously [3], the decomposition temperature of sebacic acid lies beyond the temperature range in which its polycondensation with ethylene glycol was carried out, but, in this case also, there was an appreciable amount of carbon dioxide formed at lower temperatures. Of the dicarboxylic acids studied, sebacic acid had the highest thermal stability, and this characteristic was fully preserved also in the polycondensation process, as can be seen from Fig. 6, which shows the variation of the molecular weight of polyethylene sebacate, and of the amount of the carboxyl groups eliminated, with the temperature of the polycondensation of sebacic acid with ethylene glycol. With increase in reaction temperature from 230° to 280°, although there is an increase in the amount of carbon dioxide evolved, this attains only 0.023%, i.e., very much less than for the other acids. For this reason the molecular weight rises continuously over the temperature range studied.

In accordance with this behavior, the values of the molecular weights determined from the viscosity of a polyester solution and by carboxyl groups are not appreciably different, which is in contrast with the behavior of the other dicarboxylic acids studied.

As already noted, in all cases the decomposition of dicarboxylic acids during the process of their polycondensation with glycols occurs at lower temperatures than the decomposition of the acids themselves. We consider that the cause of this phenomenon is that the terminal carboxyl groups of the polyester macromolecules are lower in thermal stability than the carboxyl groups of the dicarboxylic acids. This conclusion is confirmed by the high rate at which the discrepancy between the molecular weight determined from viscosity and the molecular weight determined from carboxyl end groups increases with rise in temperature. As the terminal carboxyl groups become destroyed, their determinable amount naturally becomes less and less, and the molecular weight calculated on this basis, therefore, rises proportionally. If, however, preferential decomposition of the carboxyl groups of dicarboxylic acids occurred, then there would inevitably be an accumulation of hydroxyl groups. Thus, in the decomposition of succinic and sebacic acids the main products are cyclic compounds, and the blocking of hydroxyl groups by decomposition products of the acids cannot occur. In this case the molecular weight determined from terminal hydroxyl groups should be correspondingly less than that determined from the viscosity of a polyester solution, whereas in actual fact the difference between their values was small. On the other hand, the elimination of terminal carboxyl groups with evolution of carbon dioxide leads to the formation of nondeterminable terminal alkyl groups, and such a concept is in accord with the observed facts.

SUMMARY

1. A study has been made of the effect of temperature on the polycondensation of ethylene glycol with oxalic, malonic, succinic, adipic, and sebacic acids.

2. It has been found that in presence of ethylene glycol the process of decarboxylation is greatly accelerated, and as a result no polyester is formed at all in the case of oxalic and malonic acids, and in the case of succinic and adipic acids the molecular weight of the resulting polyester falls as the reaction temperature rises.

3. It has been found that in presence of glycols the decarboxylation temperatures of dicarboxylic acids are greatly lowered.

4. It has been established that the evolution of carbon dioxide results from the breakdown of the terminal carboxyl groups of the polyester molecule.

5. It has been shown that the breakdown of terminal carboxyl groups hinders the normal course of the polycondensation and leads to the formation of polyesters of lower molecular weight.

Received March 25, 1953

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MACROMOLECULAR COMPOUNDS

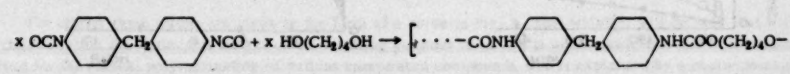
COMMUNICATION 63. EFFECT OF VARIOUS FACTORS ON THE COPOLYMERIZATION OF DIISOCYANATES AND GLYCOLS

V. V. Korshak and I. A. Gribova

As long ago as 1887, Solonitsa discovered for the first time the ability of various monomers to enter into copolymerization reactions [1]. He found that allyl esters and sulfur dioxide were able to copolymerize with the formation of macromolecular compounds, namely the polysulfones [1, 2]. Copolymerization reactions of this sort — sometimes called, not altogether appropriately, heteropolymerization [3] — have not received much investigation, and the laws governing them have not yet been studied in detail. Particularly little study has been devoted to the copolymerization of diisocyanates with glycols, which results in the formation of polyurethans, the polyamidoesters of carbonic acid [4].

Lieser and Macura [5], Bayer and coworkers [6, 7], and Hochtlen [8] have described the conditions for reaction between di- or tri-isocyanates and polyhydric alcohols, and have characterized the properties of the products. Strepikheev, Artemyev, and Shmidt [9] have investigated the effect of the nature of the glycol and solvent and of the proportions of starting materials on the properties of the product of this reaction. As a result of these investigations, much has become known concerning the conditions for the preparation of the products of this reaction, their properties, and their fields of application. But the general picture of the reactions occurring and their mechanism has remained almost without consideration. It was with the object of elucidating these questions that the present investigation was undertaken. Our results have already been published in part [10, 11].

We have studied the reaction of copolymerization between methylenedi-p-phenylene diisocyanate and 1,4-butanediol, the products of which are soluble in nitrobenzene, so that it was possible to carry out the whole process from beginning to end in a homogeneous medium and so avoid the difficulties associated with the investigation of reactions occurring in a heterogeneous system:



First of all we determined the effect of the duration of heating on the specific viscosity of the reaction solution at 145°. A solution of equimolecular amounts of methylenedi-p-phenylene diisocyanate and 1,4-butanediol in nitrobenzene was heated in an Ostwald viscometer, and at definite intervals of time, the time of flow was determined and the specific viscosity of the solution calculated. The results obtained are given in Table 1.

TABLE 1

Change in the Specific Viscosity of the Reaction Solution with Time

Duration of heating (mins.)	Specific viscosity of solution having concentration shown (mole/liter)			
	0.0973	0.151	0.175	0.196
30	0.034	0.085	0.164	0.228
60	0.044	0.137	0.257	0.344
90	—	—	0.351	0.474
120	0.091	0.220	0.433	0.579
180	0.129	0.287	0.591	0.831
240	0.170	0.322	0.690	1.047
300	0.176	0.348	—	1.163
330	—	—	0.790	—
360	0.202	0.363	0.836	Precipitate formed
420	0.228	0.363	—	—

From the data in Table 1 the graphs in Fig. 1 were constructed. They show that for the polymers formed there is an increase in molecular weight with time.

In order to determine the effect of the duration of the reaction on the molecular weight of the polymer formed, experiments were carried out in which test samples were taken at definite intervals of time and their molecular weights determined from viscosity measurements in solution. The results are given in Table 2 (concentration of the diisocyanate 0.352 mole/liter; equimolecular proportions; nitrobenzene solvent).

As can be seen from Fig. 2, the difference in the molecular weights of the products obtained at 145° and at 155° is at first

TABLE 2

Change of Molecular Weight with Time

Duration of heating (min)	Reaction temperature (°C)			
	145		155	
	specific viscosity of 0.5% solution in 85% phenol	mole weight	specific viscosity of 0.5% solution in 85% phenol	mole weight
30	0.082	55,000	0.105	6,500
60	0.109	6,700	0.134	8,300
90	0.132	8,200	0.153	9,500
180	0.167	10,300	0.212	13,200
240	0.183	11,400	0.252	15,500
300	0.203	12,600	0.244	15,200
360	0.238	14,600	0.259	16,000
420	0.260	16,700	0.266	16,500
480	0.287	17,800	0.245	15,100
600	0.309	19,200	0.253	15,700

such that at the higher temperature a polyurethan of higher molecular weight is formed. After six hours, however, the picture has changed, and the product obtained at the lower temperature has the higher molecular weight. This is evidently associated with the greater prominence at higher temperatures of destructive reactions, which curtail the growth of the molecules.

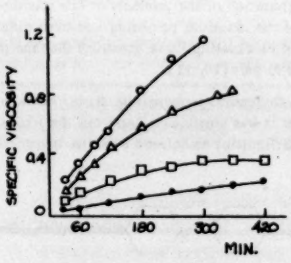


Fig. 1. Dependence of the specific viscosities of reaction solutions of various concentrations on the duration of the reaction: o = 0.196 mole/liter; Δ = 0.175 mole/liter; □ = 0.151 mole/liter; ● = 0.0973 mole/liter.

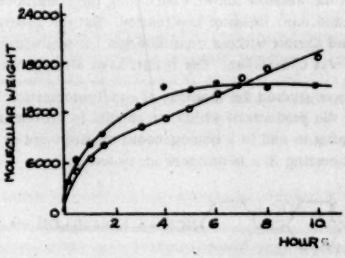


Fig. 2. Dependence of the molecular weights of polyurethans on the duration of the reaction: ● = at 155°; o = at 145°.

The effect of temperature on the rise in the molecular weights of polyurethans was studied over the range 103-184°, equimolecular amounts of the starting materials being heated together for a given time (six hours) in nitrobenzene solution (the amount of nitrobenzene was ten times the total amount of reactants). The results are given in Table 3.

As will be seen from the graph in Fig. 3, the molecular weight is greatly dependent on the reaction temperature for a given time of heating. The products obtained in the temperature range 145-155° have the greatest molecular weight. At lower temperatures, owing to the low reaction rate, the process does not appear to go to completion, and at higher temperatures the part played by destructive reactions comes into prominence, resulting in a fall in the molecular weight of the product.

The above results were obtained for reactions in which the starting materials were taken at one particular concentration. At other concentrations considerable differences in the results may be expected. Experiments were, therefore, performed in which the starting materials, still taken in equimolecular proportions, were taken in concentrations varying from 0.027 to 0.24 g per g of solvent. The reaction was carried out for six hours at 165°. The results are given in Table 4.

TABLE 3

Dependence of the Molecular Weight of the Polyurethans on the Reaction Temperature

Reaction temp. (°C)	Properties of polyurethan	
	sp. viscosity of 0.5% soln. in 85% phenol	mole weight
103	0.191	12,000
125	0.231	13,000
140	0.280	17,700
145	0.448	27,000
150	0.425	26,500
155	0.344	21,700
165	0.273	16,100
184	0.181	11,600

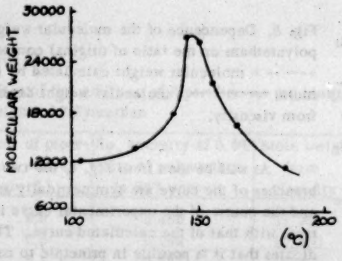


Fig. 3. Dependence of the molecular weight of the polyurethan on the reaction temperature.

TABLE 4

Effect of the Concentration of the Starting Materials on the Molecular Weight of the Polyurethan

Concn. of reactants in soln. (g per g of nitrobenzene)	Sp. viscosity of 0.5% polyurethan in 85% phenol	Mole weight of polyurethan
0.039	0.124	7,700
0.055	0.180	10,800
0.084	0.271	16,100
0.150	0.387	24,300

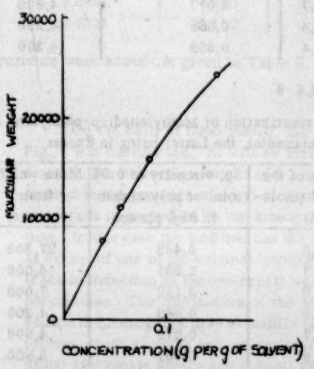


Fig. 4. Dependence of the molecular weight of the polyurethan on the concentration of the reactants in the solution.

For clarity these results are given in the form of a curve in Fig. 4, from which it will be seen that with increase in concentration the molecular weight of the resulting polymer rises. As is well known, this sort of relationship is observed for the radical polymerization of various unsaturated compounds, and is explained by a chain-propagation reaction with participation of solvent molecules [12]. In the case of the copolymerization of diisocyanates with glycols, such a reaction is impossible. The cause of the lower molecular weights of polyurethans obtained in dilute solutions may be, to some extent, the reduced reaction rate resulting from the reduction in the frequency of collisions between reactant molecules, and we may also expect an intensification of side reactions such as the decomposition of butanediol into water and tetrahydrofuran, which will lead to disturbance of the equimolecular ratio of reactants and to proportional reduction in the molecular weight of the polymer, as will be shown below.

The copolymerization reaction between diisocyanates and glycols, like every other reaction in which two components take part, will be sensitive to the proportion of starting materials. One of us has previously shown that in the polycondensation of dicarboxylic acids with diamines [13] and with glycols [14], in the reaction of dihydrazines with dialdehydes [15], and in the polycondensation of dihalo derivatives with aromatic hydrocarbons [16], the molecular weight of the resulting polymer is at its maximum only when the original substances are in equimolecular proportions, and, when one component is in excess, it falls proportional to the amount of this component. Strepikheev, Artemyev, and Shmidt [9] showed that in the case of the copolymerization of hexamethylene diisocyanate with 1,4-butanediol, the polymer of maximum molecular weight is obtained when the original components are in equivalent proportions. The curve that they obtained, however, was unsymmetrical, and this prompted us to verify this relationship for methylenedi-p-phenylene diisocyanate. The reaction was carried out at 145° in a solution containing one part of reactants and ten parts of nitrobenzene. The results are given in Tables 5 and 6.

The results are shown in Fig. 5, in which the continuous line indicates the molecular weight found, and the broken line the molecular weight calculated.

TABLE 5

Copolymerization of 1,4-Butanediol with Methylenedi-p-phenylene Diisocyanate, the Latter being in Excess

Excess of the diisocyanate (mole-%)	Sp. viscosity of 0.5% solution of polyurethan in 85% phenol	Mole weight, from viscosity	Mole weight, calculated*
0.0	0.448	27,000	∞
11.6	0.190	11,900	3,190
17.4	0.113	9,100	2,200
24.3	0.094	5,800	1,650
48.7	0.077	4,800	950
65.4	0.068	4,200	770
100.4	0.069	4,300	590

TABLE 6

Copolymerization of Methylenedi-p-phenylene Diisocyanate with 1,4-Butanediol, the Latter being in Excess

Excess of the glycol (mole-%)	Sp. viscosity of 0.5% soln. of polyurethan in 85% phenol	Mole weight, from viscosity	Mole weight, calculated*
0.5	0.442	27,300	68,000
10.7	0.231	14,000	3,260
20.9	0.112	7,000	1,700
40.2	0.069	4,200	930
50.7	0.073	4,600	760
100.9	0.061	3,800	430

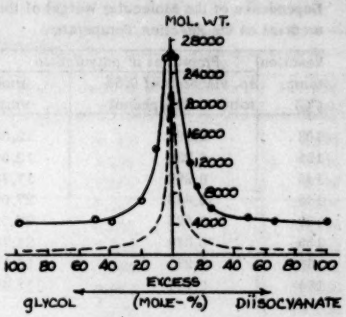


Fig. 5. Dependence of the molecular weight of polyurethans on the ratio of original components: ------ = molecular weight calculated by formula; ———— = molecular weight determined from viscosity.

As will be seen from Fig. 5, the two branches of the curve are symmetrically arranged and the course of the experimental curve is identical with that of the calculated curve. This indicates that it is possible in principle to calculate the molecular weight of polyurethans beforehand from the excess of one of the components.

An interesting peculiarity of the polyurethans obtained with an excess of diisocyanate is that various values of molecular weight are obtained, depending on the method by which the polymer is isolated. When the solvent is distilled off in steam, polyurethans of higher molecular weight are obtained than when the solvent is removed by washing the resin with alcohol or acetone. Table 7 shows that values of the molecular weight found for polyurethans in the same experiment, in which part of the reaction mixture was treated with alcohol, and part with steam.

These differences in molecular weight probably arise from the fact that the hydrolysis of isocyanate groups yields amino groups, which react with unchanged isocyanate groups. As a result, polyurethans are obtained containing urea groupings in the chain and having a higher molecular weight.

$$\cdots -O(CH_2)_4OCONHC_6H_4CH_2C_6H_4NH - CO - NHC_6H_4CH_2C_6H_4NHCOO(CH_2)_4O- \cdots$$

As Strepikheev, Artemyev, and Shmidt [7] showed, diisocyanates react so rapidly with diamines, that the process is reminiscent of ionic reactions and can even occur in an aqueous medium. There is, therefore, nothing surprising in the formation of polyurethan-polyureas that we have found to occur. It is probably to the formation of these that the lack of symmetry of the curve obtained by the above authors must be attributed.

When we had investigated the effect of the proportions of the original reactants on the molecular weight of the polyurethan, there arose the question of how the molecular weight is affected by the addition of a monofunctional substance able to react with isocyanate groups. In order to determine this effect we have investigated the reaction in which the diisocyanate and glycol were taken in equivalent proportions and various amounts of such monofunctional compounds as octyl alcohol and piperidine were added. In other respects the reaction was carried out under the same conditions as before. The results of these experiments are given in Tables 8 and 9.

* The calculated molecular weight was found from the formula:

$$M = \frac{100(M_a + M_b)}{q} + M_a,$$

(M_a and M_b are the molecular weights of the original components; q is the excess of the component a in molar percent).

TABLE 7

Effect of the Method of Treatment of the Polyurethan on its Molecular Weight

Expt. No.	Molecular weight of polyurethan treated by	
	washing with alcohol	distilling off solvent in steam
11	15,100	16,900
12	6,600	8,700
15	13,100	21,300

On the basis of these results, the curve in Fig. 6 was constructed.

TABLE 8

Effect of the Addition of n-Octyl Alcohol on the Molecular Weight of Polyurethan

Amt. of octyl alcohol added (mole-%)	Sp. viscosity of 0.5% soln. of polyurethan in 85% phenol	Mole weight, from viscosity	Mole weight, calculated
0.0	0.428	27,000	∞
0.9	0.163	10,300	37,910
2.0	0.145	9,900	17,130
5.2	0.175	10,800	6,670
10.0	0.106	6,400	3,530
22.6	0.080	4,800	1,630
53.9	0.050	3,100	796

The results of experiments in which various amounts of piperidine were added are given in Table 9.

TABLE 9

Effect of the Addition of Piperidine on the Molecular Weight of Polyurethan

Amt. of piperidine added (mole-%)	Sp. viscosity of 0.5% soln. of polyurethan in 85% phenol	Mole weight, from viscosity	Mole weight, calculated
0.0	0.450	27,000	∞
2.5	0.162	10,400	13,730
5.1	0.147	8,900	6,770
10.0	0.120	7,200	3,480
20.1	0.075	4,800	1,780
29.4	0.051	3,200	1,220
55.7	0.044	2,800	760

On the basis of these results, the curve in Fig. 7 was constructed. As will be seen from Figs. 6 and 7, the molecular weight of a polyurethan formed in the presence of octyl alcohol or piperidine falls in proportion to the amount of the addition. In this case the addition has the same effect as excess of one of the original components, and leads to reduction in the molecular weight of the polyurethan. The mechanism of the action of the additives investigated may evidently be stated as follows: both alcohols and amines react with terminal isocyanate groups and convert them into groups that are inactive in this reaction, so preventing the further growth of the polymer.

Polyurethans belong to the group of heterochain polyamidoesters, and they have amide and ester linkages in their molecules, and these, as one of us has already shown in collaboration with Zamyatina [17] and with Golubev [14], are readily broken down as the result of aminolysis under the action of diamines, acidolysis under the action of mono- and di-carboxylic acids, and alcoholysis under the action of alcohols, glycols, and other reagents able to react with amide or ester linkages. As a result of these reactions, polyesters and polyamides undergo degradation. Since the polyurethan molecule contains amide and ester linkages, it might be expected that polyurethans would also be degraded under the influence of glycols, acids, amines, and isocyanates, and that this phenomenon occurring in the course of the process should affect the result of the reaction. In order to elucidate this question, we have investigated the action of 1,4-butanediol, adipic acid, aniline, and phenyl isocyanate on polyurethan.

The glycolysis of polyurethan was studied for the product obtained from equimolecular amounts of methylenedi-p-phenylene diisocyanate and 1,4-butanediol. This polyurethan was heated with various amounts of 1,4-butanediol in nitrobenzene solution at 170°, and test samples were taken at definite intervals of time; the molecular weights of these were determined from their viscosities (0.5% solution in 85% aqueous phenol). The results are given in Table 10.

On the basis of these results, the curves given in Fig. 8 were constructed; they show the way in which the molecular weight of the polyurethan varies with time when it is heated with various amounts of 1,4-butanediol.

As will be seen from Fig. 8, the degree of degradation rises with increase in the amount of the degrading agent (1,4-butanediol) taken. An important feature of this process is indicated by the fact that, when the polyurethan is heated in nitrobenzene solution in absence of 1,4-butanediol, degradation still occurs, although to an appreciably less extent. In the experiments with 1,4-butanediol, it is probably necessary to take into account also degradation due to thermal action or oxidation by nitrobenzene.

In separate experiments the polyurethan was heated with ten times its weight of ethylene glycol for six hours, and after this degradation treatment its molecular weight was found to be 7670 (originally 26,300). Another sample

of polyurethan of molecular weight 29,300 was heated with ten times its weight of 1,4-butanediol, and its molecular weight fell to 8500.

The tendency of polyurethans to undergo acidolysis was established by heating a sample of polyurethan of molecular weight 29,300 with ten times its weight of adipic acid. After six hours the molecular weight had fallen to 4900.

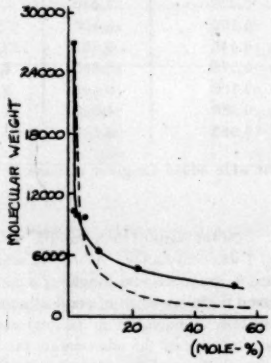


Fig. 6. Effect of additions of octyl alcohol on the molecular weight of the polyurethan: ------ = molecular weight calculated by formula; ——— = molecular weight determined from viscosity.

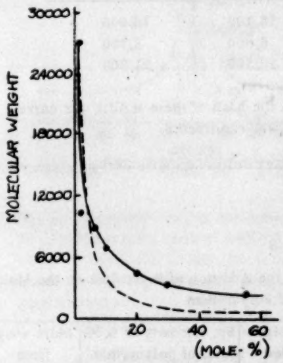


Fig. 7. Effect of additions of piperidine on the molecular weight of the polyurethan: ------ = molecular weight calculated by formula; ——— = molecular weight determined from viscosity.

TABLE 10

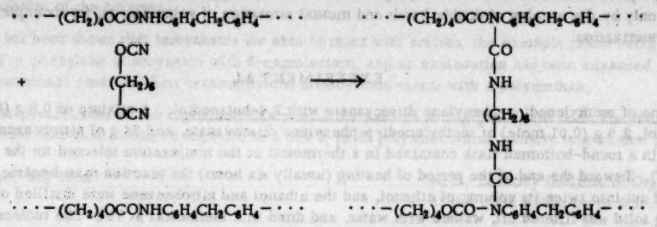
Kinetics of the Degradation of Polyurethan with 1,4-Butanediol

Duration of heating (min)	Control expt.		Addition of 12.4% 1,4-butanediol		Addition of 33.5% 1,4-butanediol		Addition of 50.8% 1,4-butanediol	
	sp. viscosity of 0.5% soln.	mole weight	sp. viscosity of 0.5% soln.	mole weight	sp. viscosity of 0.5% soln.	mole weight	sp. viscosity of 0.5% soln.	mole weight
0.0	0.249	15,600	0.249	15,600	0.249	15,600	0.249	15,600
15	0.201	12,200	–	–	–	–	–	–
30	0.190	11,500	–	–	–	–	–	–
60	0.164	10,200	0.157	10,000	0.141	8,600	0.139	8,400
120	0.164	10,200	0.142	8,000	0.134	8,200	–	–
180	0.159	10,100	0.141	8,700	0.123	7,700	–	–
240	–	–	–	–	5.109	6,700	0.083	5,200
300	0.168	10,500	0.129	7,900	0.110	6,700	–	–
360	–	–	0.122	7,800	–	–	–	–

The aminolysis of polyurethans was carried out by heating a sample of polyurethan with aniline for six hours; the molecular weight fell from 26,000 to 2800. The isocyanolysis of polyurethan was carried out by heating it with phenyl isocyanate. The polyurethan dissolved completely, and no precipitate was formed when the solution was poured into benzene, evidently because the macromolecules had been completely destroyed and converted into a product of low molecular weight.

Attempts to effect isocyanolysis by means of hexamethylene diisocyanate resulted in the formation of an infusible insoluble product, whose molecular weight could not be determined. It may be supposed that in this case, in addition to degradation, there occurred cross-linking of the polyurethan macromolecules with formation of a three-dimensional product, which, like all compounds of that type, was infusible and insoluble. Such cross-linking may

occur as a result of the reaction of hexamethylene diisocyanate with hydrogens of amide groups in accordance with the scheme:



In order to make sure that such a reaction is possible, we examined the possibility of a process of this type in the case of the reaction of methylenedi-p-phenylene diisocyanate with 6-caprolactam (2-oxohexamethylenimine). It was found that these substances readily react together, forming an addition product by interaction of isocyanate and amide groups, namely 1,1'-[(methylenedi-p-phenylene)dicarbamoyl]bis(2-oxohexamethylenimine). This result confirms our supposition concerning the mechanism of the formation of the three-dimensional polymer in the reaction of polyurethan with a diisocyanate. In this case, a determining part is played by the reactivities of the diisocyanate and the polyurethan. Thus, methylenedi-p-phenylene diisocyanate and the polyurethan prepared from it do not form a three-dimensional polymer, and as a result it is found possible to carry out the copolymerization reaction with any desired excess of the diisocyanate. This same polyurethan readily reacts with hexamethylene diisocyanate, as we have seen above, forming a three-dimensional product. It is evident that the reactivity is greater for the second pair of components than for the first, and that this explains the different results of the reaction in the two cases.

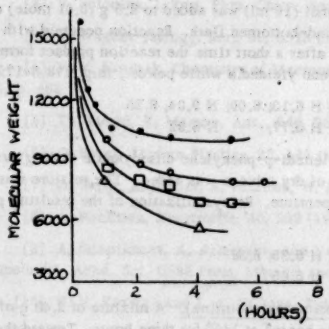


Fig. 8. Degradation of polyurethan in presence of 1,4-butanediol: Δ = 50.8 mole-% excess of 1,4-butanediol; □ = 33.5 mole-% excess of 1,4-butanediol; o = 12.4 mole-% excess of 1,4-butanediol; ● = in absence of 1,4-butanediol.

We may, therefore, conclude that polyurethans are capable of undergoing degradation reactions as a result of alcoholysis, acidolysis, aminolysis, and isocyanolysis, which occur when they are heated with substances containing alcohol, carboxyl, amine, or isocyanate groups in their molecules. We may conclude from this that such degradative reactions play a determining part also in the course of the synthesis of polyurethans by the copolymerization of diisocyanates with glycols.

In conclusion, we will discuss briefly the general characteristics of the reaction of diisocyanates with glycols leading to the formation of polyurethans. This reaction must be classified as a polymerization reaction, mainly by the criterion of the absence of elimination of a low-molecular-weight product, which is characteristic of a polycondensation process. At the same time, this reaction differs in principle from radical and ionic polymerizations, which are typical for various vinyl monomers and require the participation of initiators or catalysts. It differs essentially also from hydrolytic polymerization [18], which is characteristic for cyclic esters and amides, such as 6-caprolactam, which for their polymerization require activators such as water, acids, amines, alcohols, and similar substances having mobile hydrogen atoms [19].

The peculiarity of the copolymerization reaction between diisocyanates and glycols is the occurrence of hydrogen transfer at each stage of the process, in accordance with the scheme:

$$x\ OCNRNCO + x\ HOR'OH \rightarrow (-CONHRNHCOOR'O-)_x.$$

It is not, however, a chain reaction, since no free radicals take part in the intermediate stages, and the reaction is not initiated by peroxides and other generators of free radicals. Since we have a stable compound at every stage of the reaction and observe a continuous rise in molecular weight during the course of the reaction, we have sufficient grounds to classify this reaction as a multistage reaction.

Polymeric reactions of this type, which are associated with transfer of a hydrogen atom, may be called migrational polymerization, as distinct from polymerization of other types, which is not accompanied by hydrogen transfer, but only by the opening of double bonds and mutual saturation of valencies, as, for example, in the case of vinyl polymerization.

EXPERIMENTAL

Reaction of methylenedi-p-phenylene diisocyanate with 1,4-butanediol. A mixture of 0.9 g (0.01 mole) of 1,4-butanediol, 2.5 g (0.01 mole) of methylenedi-p-phenylene diisocyanate, and 34 g of nitrobenzene was heated under reflux in a round-bottomed flask contained in a thermostat at the temperature selected for the experiment (usually 145°). Toward the end of the period of heating (usually six hours) the reaction mass became very thick. It was poured out into twice its volume of ethanol, and the ethanol and nitrobenzene were distilled off in steam. The resulting solid was filtered off, washed with water, and dried in a thermostat at 70°. The molecular weight of the resin was determined from the viscosity of a 0.5% solution in 85% aqueous phenol. The resulting polyurethan was a white or slightly pink powder, m.p. 190-200°, readily soluble in cresol and 85% aqueous phenol, and insoluble in the usual organic solvents.

Dimethyl(methylenedi-p-phenylene)dicarbamate. Methanol (10 ml) was added to 2.5 g (0.01 mole) of methylenedi-p-phenylene diisocyanate contained in a 50-ml round-bottomed flask. Reaction occurred with the evolution of much heat. The mixture was allowed to stand, and after a short time the reaction product formed a precipitate, and was filtered off. Recrystallization from hot toluene yielded a white powder, m.p. 178.5-179.5°.

	Found %	C 65.71; 65.86;	H 6.13; 6.00;	N 9.04; 9.25
$C_{17}H_{18}O_4N_2$.	Calculated %	C 68.95;	H 5.77;	N 8.92

Diphenyl (methylenedi-p-phenylene)dicarbamate. Methylenedi-p-phenylene diisocyanate (3.48 g) was mixed with phenol (2.7 g) in a round-bottomed flask, and 10 ml of dry toluene was added. The mixture was heated at the boil for three hours and then allowed to cool to room temperature. Recrystallization of the resulting precipitate from hot toluene yielded a white powder, m.p. 168°.

	Found %	C 74.47; 74.52;	H 5.35; 5.38
$C_{27}H_{22}N_2O_4$.	Calculated %	C 73.95;	H 5.05

1,1'-[(Methylenedi-p-phenylene)dicarbamoyl]bis(2-oxohexamethyleneimine). A mixture of 2.48 g of methylenedi-p-phenylene diisocyanate and 2.25 g of ε-caprolactam was heated at 145° for three hours. Toward the end of this time the reaction mixture generally solidified. The product was recrystallized from hot benzene, and yielded a white powder, m.p. 174-175°.

	Found %	C 68.29; 67.90;	H 6.83; 7.22
$C_{27}H_{32}N_4O_4$.	Calculated %	C 68.02;	H 6.77

SUMMARY

1. A study has been made of the effect of time, temperature, concentration, ratio of original components, and addition of monofunctional compounds on the rise in molecular weight of polyurethans formed by copolymerization of methylenedi-p-phenylene diisocyanate with 1,4-butanediol. The properties of the products formed have been examined.

2. It has been shown that the molecular weight of the polyurethans increases continuously as the duration of reaction increases.

3. It has been found that the molecular weight of the polyurethans attains a maximum value in a definite temperature range; at lower or higher temperatures the molecular weight falls.

4. It has been shown that, with rise in the concentration of the solution, the molecular weight of the polyurethans rises. An explanation has been given for this phenomenon.

5. It has been shown that the dependence of the molecular weight of the polyurethans on the ratio of original components is expressed by a symmetrical curve.

6. It has been found that additions of monofunctional substances bring about a reduction in the molecular weight of the polymer obtained.

7. The possibility of obtaining mixed polyurethan-polyureas has been demonstrated.

8. It has been found that polyurethans undergo alcoholysis in presence of glycols, aminolysis in presence of amines, acidolysis in presence of acids, and isocyanolysis in presence of isocyanates. All of these reactions result in the degradation of the polymer.

9. It has been shown that isocyanates are able to react with amides, the example taken being the reaction of methylenedi-p-phenylene diisocyanate with 6-caprolactam, and an explanation has been advanced for the formation of three-dimensional products when hexamethylene diisocyanate reacts with a polyurethan.

10. The peculiarities of the copolymerization of diisocyanates with glycols have been discussed, and it is proposed that these reactions should be regarded as a new type of polymerization, namely migrational polymerization.

Received April 28, 1953

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BRIEF COMMUNICATIONS

DIPOLE MOMENTS OF SOME INTERMEDIATE PRODUCTS IN THE SYNTHESIS OF VITAMIN A

V. M. Kazakova, Ya. K. Syrkin, and A. N. Shidlovskaya

We have determined the dipole moments of some β-ionone derivatives that form intermediate products in the synthesis of vitamin A. The dielectric constants were measured by the heterodyne method in benzene solution at 25°. Table 1 gives the constants of the substances investigated, extrapolated to infinite dilution: the total polarization P, the refraction for the yellow line of sodium (R_{Na}), the orientation polarization, and, in the last column, the dipole moment. For two of the substances the refraction was measured for six wave lengths, and the value of λ_∞ was found and the exaltation of refraction calculated; the results are given in Table 2. We measured the refraction of the ethyl ester of 5-methyl-7-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6-heptatrienoic acid. We assumed that the exaltation of refraction for the methyl ester and for the acid itself would be approximately the same as for the ethyl ester (4.5 cm for the extrapolated value and 6.7 for R_{Na}). On this basis the refractions of the corresponding substances were determined.

TABLE 1

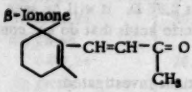
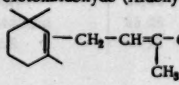
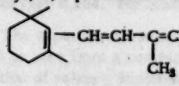
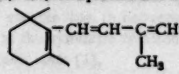
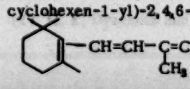
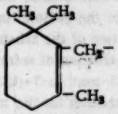
Substance	B.p. in °C (p in mm Hg)	P_∞	R_{Na}	P_{Or}	$\mu \cdot 10^{18}$
β-Ionone 	80 (0.1)	313.4	61.7	251.7	3.47
α,2,6,6-Tetramethyl-1-cyclohexene-1-crotonaldehyde (Aldehyde C_{14}) 	95 (0.3)	331.3	67.2	264.1	3.56
3-Methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4-pentadien-1-ol (Alcohol C_{15}) 	100 (10^{-3})	161.7	70.7	91	2.09
5-Methyl-7-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6-heptatrienoic acid 	B.p. 158-159°	257.1	87.1	170.0	2.85
Methyl ester of 5-methyl-7-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6-heptatrienoic acid 	125 (10^{-3})	267.9	90.6	177.3	2.92

TABLE 2

Wavelength	Alcohol C_{15}	Aldehyde C_{14}
Cd orange		
6438.47	69.10	66.94
Hg yellow		
5790.66	70.87	67.25
Hg green		
5460.71	71.17	67.60
Cd green		
5085.82	71.88	67.86
Cd blue		
4799.91	72.38	68.19
Cd blue		
4678.15	72.53	68.54
R_{CD} extrapolated	67.3	63.5
R_{CD} additive		
ΔR	0.6	1.8

As is well known, transition from formaldehyde to acetaldehyde is accompanied by an appreciable increase in dipole moment (from 2.27 to 2.72 D (in the vapor)). This is associated with increase in the negative charge on the oxygen at the expense of the hydrogens of the methyl group. It is further known that the conjugation of the carbonyl bond with the double bond C=C also leads to a considerable rise in the moment. Thus, in benzene solution acrolein has a moment of 2.28 D and methacrylaldehyde a moment of 2.72 D, which is considerably higher than that of acetaldehyde in solution (2.56 D). In the substances that we have investigated, these regularities are manifested more strongly. In Aldehyde C_{14}, the moment is considerably enhanced in comparison with methacrylaldehyde (3.58 instead of 2.72 D). In this we have a hydrogen of methacrylaldehyde replaced by an apparently nonpolar group.



The moment of Alcohol C_{15} (2.09 D in solution) is higher than that of allyl alcohol (1.63 D in the vapor). Whereas the polarity of allyl alcohol with its one double bond does not differ from that of the usual alcohols, the presence of the additional double bond and methyl group in Alcohol C_{15} results in an appreciable increase in moment. The dipole moments of formic and acetic esters (from methyl to pentyl) lie in the range 1.8-1.9 D. The introduction of a chain of four conjugated C=C bonds leads to an increase in moment of about 1 D. It should be noted that acids in the dimeric state have reduced moments. In our case, at concentrations of about 0.0015, the moment of 5-methyl-7-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6-heptatrienoic acid is 2.85 D. It will be seen that the moment of this molecule is greater by about 1.2 D than the moments of monomeric acids that do not contain a double bond.

The authors express their gratitude to G. I. Samokhvalov for providing the preparations investigated.

Received February 16, 1954

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MOLAR REFRACTIONS AT VARIOUS WAVELENGTHS OF SUBSTANCES HAVING CONJUGATED BOND SYSTEMS

G. G. Kikina, Ya. K. Syrkin, and E. A. Shott-Lvova

Refraction, as is well-known, is a property for which additivity rules are satisfactorily obeyed. In order to elucidate the significance of departures from additivity, it is necessary to know the refraction extrapolated to infinitely long waves. For this purpose the refractive index must be measured at various wavelengths, and extrapolation must then be performed by a well-known formula in order to find R_∞. We have made measurements on eight substances (benzene, naphthalene, anthracene, phenanthrene, acenaphthene, triphenylmethane, p-benzoquinone, and phenanthrenequinone) at seven wavelengths, from 4046.56 to 6439.47 A. In the table we give the wavelength (first column), values of the refraction for the various substances at the various wavelengths, the extrapolated values of

Wavelength A	Refraction of							
	benzene	naphthalene	anthracene	phenanthrene	acenaphthene	triphenylmethane	p-benzoquinone	phenanthrenequinone
4046.56 Hg violet	27,41	47.56	74,85	68.98	56,11	85,47		
4678,15 Cd blue	26,75	46.54	70,58	67,42	54,77	83,43		
4799,91 Cd blue	26,57	46.29	70,15	67,16	54,47	83,02		
5085,82 Cd green	26,47	45,66	68,97	66,01	53,75	82,46	30,06	
5460,74 Hg green	26,27	55,17	67,68	65,12	53,15	81,83	29,67	75,74
5790,66 Hg yellow	26,12	44,77	66,97	64,54	52,67	81,45	29,42	74,59
6439,47	25,90	44,18	65,50	63,45	52,03	80,80	29,02	72,71
R_∞	25,01	41.85	61,01	59.50	49.22	78,06	27.45	66.04
R_∞ additive	25,28	40.00	54,72	54,72	46.89	76,09	25.87	55,31
ΔR	−0.27	1.85	6.29	4.78	2.33	1,97	1.58	10,73

the refraction (third line from the bottom), the additive values of the refraction extrapolated to infinitely long wavelength, and finally the difference $R_\infty - R_{\infty\,add} = \Delta R$, i.e., the exaltation of refraction calculated by a comparison of R_∞ with the additive value for λ_∞ the following values were assumed: H 1.068, C 2.373, double bond 1.546, carbonyl oxygen 2.134. For molecules without conjugated bonds these values are correct within 0.015.

The experimental results indicate a rapid rise in ΔR with increase in the number of conjugated C=C bonds, as will be seen from a comparison of naphthalene with anthracene and p-benzoquinone with phenanthrenequinone. Distortion of valency angles and change in interatomic distances affects ΔR. This follows from a comparison of naphthalene with acenaphthene. "Acenes" and "phenes" having the same number of CC bonds apparently have different ΔR values. This is indicated by a comparison of anthracene and phenanthrene. It is interesting that in triphenylmethane, in spite of the apparent absence of conjugation between the phenyl groups, the exaltation is considerably greater than in benzene. Substances of quinone structure have a high exaltation of refraction. Attention is drawn to the symbatic relationship between the enhanced exaltations of refraction and the low excitation energies of the triplet state [1].

Received February 16, 1954

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SYNTHESIS OF THIOPHENE DERIVATIVES CONTAINING THE tert-BUTYL GROUP, AND SOME OF THEIR PROPERTIES

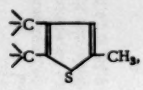
Ya. L. Goldfarb and I. S. Korsakova

As is well known, the method of alkylation by means of alkyl halides in presence of catalysts of the aluminum chloride type is of little use for the preparation of thiophene homologs from unsubstituted thiophene [1]. An exception is formed by the formation of 2,5-di-tert-butylthiophene in good yield (about 80%) by the action of tert-butyl chloride on thiophene in presence of a catalytic amount of ferric chloride [2]. It would appear that, in this case, the rate of alkylation of thiophene is considerably higher than that of its polymerization, which is promoted by catalysts of this type and is often accompanied by far-reaching breakdown of the thiophene.

In the course of investigations that we are carrying out on thiophene derivatives, the need arose for substituted thiophenes containing a tert-butyl group in the β-position of the thiophene ring. For their synthesis we have used the method already tried for unsubstituted thiophene of alkylation with tert-butyl chloride in presence of ferric chloride. The mixtures formed by the action of tert-butyl chloride and monosubstituted (2-methyl- and 2-ethyl-) thiophenes consisted mainly of mono- and di-tert-butylated products. The alkylation products were separated by vacuum fractionation, followed sometimes by distillation at atmospheric pressure.

From tert-butylmethylthiophene (formed under the conditions indicated from 2-methylthiophene) an aldehyde was prepared by the method described by Messina [3], and it gave a semicarbazone of m.p. 215°. According to the results of this investigator, the melting point of the semicarbazone of 5-tert-butyl-2-thiophenecarboxaldehyde is 215-216°. It may, therefore, be presumed that, when tert-butyl chloride reacts with 2-methylthiophene in presence of ferric chloride, substitution occurs in the 5-position. Of the two possible structures (I and II)

(I)



(II)

in which $-C\!\!\!\!\diagup$ is $-C(CH_3)_3$

the di-tert-butylation product of 2-methylthiophene must be assigned the structure I, since the formation of a product of structure II by the alkylation under these conditions of 2-tert-butyl-5-methylthiophene is improbable owing to steric hindrance.

In this connection it should be noted that among the reaction products from thiophene or 2,5-dimethylthiophene and a large excess of tert-butyl chloride in presence of ferric chloride no tri-, or, still more, tetra-substituted thiophenes could be isolated. Finally, if we may seek a parallel in the benzene series, we may mention that o-di-tert-butylbenzene has not been described.

Brown and coworkers [4], in a number of recently published papers on "sterically strained" systems, have come to the conclusion that the preparation of this hydrocarbon by the Friedel-Crafts method is impossible.

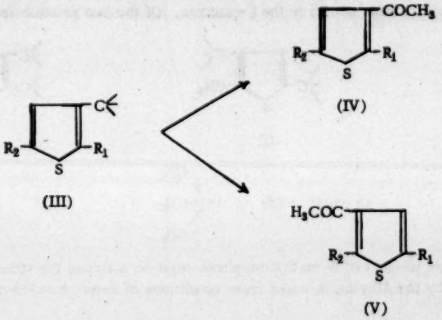
The alkylation of 2-ethylthiophene with tert-butyl chloride in presence of ferric chloride leads, as in the case of 2-methylthiophene, to the formation of two compounds. Judging from their compositions, and taking the results on the alkylation of 2-methylthiophene into account, we may assign the structures of 2-tert-butyl-5-ethylthiophene and 3,5-di-tert-butyl-2-ethylthiophene to these compounds. Alkylation of 2,5-dimethyl- or 2,5-diethyl-thiophene with tert-butyl chloride under the conditions already indicated gives only one product, containing one tert-butyl group (3-tert-butyl-2,5-dimethylthiophene or 3-tert-butyl-2,5-diethylthiophene) in high yield (90-95%).

Since they are trisubstituted thiophenes, these compounds should acylate in the β-position with formation of fully substituted thiophenes. However, when the ketone formed by the action of acetyl chloride on 3-tert-butyl-2,5-dimethylthiophene in presence of stannic chloride was investigated, it was found that it corresponded in composition to the formula $C_8H_{10}OS$, whereas for the "normal" course of the process a ketone of composition $C_{12}H_{18}OS$ should be formed. This fact can only be explained on the assumption that a tert-butyl group is eliminated when acetyl chloride acts on 3-tert-butyl-2,5-dimethylthiophene under our conditions (see experimental part).

When this process was studied further it was found that the ketone formed was, in fact, identical with the ketone that we prepared by the acetylation of 2,5-dimethylthiophene, which we established by comparison of the melting points of the oximes. Our experiments showed that similar elimination of a tert-butyl group occurred in the acetylation in presence of stannic chloride of other trisubstituted thiophenes containing a tert-butyl group that we prepared, namely, 3-tert-butyl-2,5-diethylthiophene, 3,5-di-tert-butyl-2-methylthiophene, and 3,5-di-tert-butyl-2-ethylthiophene, which yielded, respectively, 2,5-diethyl-3-thienyl methyl ketone, 5-tert-butyl-2-methyl-3-thienyl methyl ketone, and 5-tert-butyl-2-ethyl-3-thienyl methyl ketone. In all of these cases the tert-butyl group was eliminated from the β-position, which is evident from the fact that the ketones formed were found to be identical with the ketones obtained from the corresponding α,α'-disubstituted thiophenes (Table 2). In these cases also, the identity of the ketones was established by a comparison of the melting points of the corresponding derivatives and by mixture melting point tests.

Our observation concerning the elimination of the tert-butyl group from the β-position is in accord with the fact that, in the acetylation of 2,5-di-tert-butylthiophene [2] and 2-tert-butyl-5-methylthiophene, the elimination of a tert-butyl group does not occur. The elimination of a tert-butyl group in the acetylation of a system similar in nature to thiophene was recently described by Taylor and Watts [5, 6]; they found that, when p-tert-butyltoluene was treated with acetic anhydride in presence of aluminum chloride, 4'-methylacetophenone was obtained, as a result of the elimination of the tert-butyl group.

At present we do not have all of the experimental data available to enable us to make a choice between the structures IV and V for the ketones formed by the acetylation of systems of the type III:



A knowledge of the structure of these ketones, however, would enable us to make an approach to the understanding of the question, very interesting from the theoretical point of view, of the mechanism of the process of elimination of a tert-butyl group. The formation of the structure IV would indicate that direct elimination of the tert-butyl group by the CH_3CO group occurs, whereas the formation of the isomer V could be regarded as the result of attack by the CH_3CO group in the 4-position with subsequent or simultaneous elimination of the tert-butyl group.

It may be supposed that the first of these elimination processes is the more probable. This assumption of ours is in accord with the observations of Chichibabin [7], who showed that in eliminating an acetyl group a nitro group always takes up the position occupied by that acetyl group, the example that he studied being the nitration of 4'-tert-butyl-2',6'-dimethylacetophenone.

EXPERIMENTAL

Alkylation

Thiophene or its homolog was dissolved in carbon disulfide, and to this solution tert-butyl chloride and ferric chloride were added (for amounts of reactants see Table 1). The dark-brown solution was boiled and stirred for 15-20

TABLE 1

Original substance	Amount of			Compound obtained	B.p. in °C (p in mm Hg)	Yield (%)	Analysis						n_D^{20}	d_4^{20}
	original substance (g and (moles))	tert-butyl chloride (g and (moles))	solvent (CS_2) (ml)				C		H		S			
							calculated	found	calculated	found	calculated	found		
2-Methylthiophene•	30.0 (0.3)	60.0 (0.6)	170	2-tert-Butyl-5-methylthiophene••	185.5-186.5	25	70.13	70.04 70.16	9.09	9.13 9.06	20.78	20.69 20.90	1.4972	0.9391
				3,5-Di-tert-butyl-2-methylthiophene	104 (11) 238-239	60	74.28	74.10 74.19	10.48	10.43 10.41	15.23	15.50 14.89	1.4999	0.9263
2-Ethylthiophene	33.6 (0.3)	60.0 (0.6)	150	2-tert-Butyl-5-ethylthiophene	78-81 (10)	19	71.5	71.71 71.37	9.5	9.48 9.43	19.0	19.21 18.93	1.4966	0.9316
				3,5-Di-tert-butyl-2-ethylthiophene	114-115 (9)	46.5	75.0	75.29 75.34	10.71	10.77 10.90	14.29	14.46 14.02	1.5009	0.9255
2,5-Dimethylthiophene	30.6 (0.3)	30.0 (0.6)	150	3-tert-Butyl-2,5-dimethylthiophene	94-95.5 (21) 205-206	92	71.43	71.71 71.91	9.52	9.62 9.77	19.05	–	1.5014	0.9413
2,5-Diethylthiophene	15.8	16.0	70	3-tert-Butyl-2,5-diethylthiophene	110-111 (12) 235.5-236.5	85.5	73.47	73.58 73.58	10.20	10.03 10.09	16.33	16.25 16.27	1.5050	0.9392

• In each experiment the amount of ferric chloride taken was 0.02-0.04 mole.

•• This fraction was treated with N-bromosuccinimide [3] in presence of benzoyl peroxide; from the resulting substance the salt with hexamethylenetetramine was formed, and the decomposition of this with steam yielded an aldehyde, the semicarbazone of which melted, after recrystallization from alcohol, at 215°. For the m.p. of the semicarbazone of 5-tert-butyl-2-thiophenecarboxaldehyde, the literature [3] gives 215-216°. Analysis of the semicarbazone: Found %: C 53.47; 53.58; H 6.68; 6.63; S 13.75; 13.88: Calculated %: C 53.33; H 6.66; S 14.92.

TABLE 2

Starting substance	Ketone obtained	Yield (%)	B.p. in °C (p in mm Hg)	M.p. of derivative (°C)	Composition of derivative	Analysis					
						C		H		S	
						calculated	found	calculated	found	calculated	found
2,5-Dimethylthiophene	2,5-Dimethyl-3-thienyl methyl ketone•	99	108.5-109 (12.5)	A 82-83••	$C_8H_{11}NOS$ A	56.80	–	6.55	–	18.95	–
3-tert-Butyl-2,5-dimethylthiophene	2,5-Dimethyl-3-thienyl methyl ketone	55	103.5-106 (11)	A 82-83	$C_8H_{11}NOS$ A	–	56.87 57.15	–	6.42 6.42	–	19.00 18.62
2,5-Diethylthiophene	2,5-Diethyl-3-thienyl methyl ketone•••	76	123-124 (11.5)	B 167-168 C 147-148	$C_{11}H_{17}N_3OS$ B	55.23	–	7.11	–	13.38	–
3-tert-Butyl-2,5-diethylthiophene	2,5-Diethyl-3-thienyl methyl ketone	45	123-124 (11)	B 167-168 C 147-148	$C_{11}H_{17}N_3OS$ B	–	55.61 55.40	–	7.21 6.98	–	13.15 13.12
2-tert-Butyl-5-methylthiophene	5(or 2)-tert-Butyl-2(or 5)-methyl-3-thienyl methyl ketone	86	122-122.5 (10)	B 219-220 C 158.5-159.5	$C_{17}H_{26}O_4N_4S$ C	54.25	–	5.36	–	8.50	–
3,5-Di-tert-butyl-2-methylthiophene	5(or 2)-tert-Butyl-2(or 5)-methyl-3-thienyl methyl ketone	63	123-124 (11)	B 219-220•••• C 158-159	$C_{17}H_{26}O_4N_4S$ C	–	54.30 54.37	–	5.42 5.30	–	8.76 8.52
2-tert-Butyl-5-ethylthiophene	5(or 2)-tert-Butyl-2(or 5)-ethyl-3-thienyl methyl ketone	86	127-128 (9)	B 175 C 152-153	$C_{13}H_{21}N_3OS$ B	58.43	–	7.86	–	11.99	–
2,5-Di-tert-butyl-2-ethylthiophene	5(or 2)-tert-Butyl-2(or 5)-ethyl-3-thienyl methyl ketone	55.5	129-129.5 (10)	B 177 C 152-153	$C_{13}H_{21}N_3OS$ B	–	58.89 58.58	–	7.85 7.82	–	12.15 11.75

A = oxime; B = semicarbazone; C = 2,4-dinitrophenylhydrazone

• Literature [8] gives b.p. 125-128° (28 mm);

•• Literature [9] gives m.p. 83°.

••• Literature [10] gives b.p. 126-128° (12 mm), m.p. of semicarbazone 167°.

•••• With rapid heating, and m.p. 214-215° with slow heating.

hours, until the evolution of hydrogen chloride almost ceased. The dark-colored reaction mixture was then cooled with ice and decomposed by stirring with water. The solution then became yellow; there was a certain amount of resin on the bottom of the flask. The carbon disulfide layer was separated and washed with 10% HCl, 10% NaOH, and water. The washing waters and the original aqueous layer were extracted with ether, and the ether extract was washed and added to the carbon disulfide solution. The solution was dried over $CaCl_2$, the solvent was distilled off, and the residue was vacuum-fractionated and then, if necessary, distilled under atmospheric pressure. The results are given in Table 1.

Acetylation

To a well stirred and ice-cooled (to 0°) solution of the alkylthiophene and acetyl chloride (excess over the theoretical amount of 0.1 of a molecular proportion) in benzene (1:10), a solution of an equimolecular amount of stannic chloride in benzene (1:1) was added carefully and dropwise, at such a rate that the temperature in the flask did not rise above 0°. As soon as the first drops of stannic chloride were added, the solution became red, or sometimes orange. When the whole of the stannic chloride had been added, the dark-red reaction mixture was stirred at room temperature for 4-5 hours. It was then cooled externally with snow, and decomposed by dropwise addition of acidified water (3 ml of concentrated HCl in 30 ml of water). The solution then became yellow. The benzene layer was separated, washed with 10% solutions of HCl and sodium carbonate, washed with water, and dried over calcined $MgSO_4$. The benzene was distilled off, and the residue was vacuum-fractionated. The results are given in Table 2.

SUMMARY

1. The conditions have been determined for the alkylation with tert-butyl chloride of 2-methylthiophene, 2-ethylthiophene, 2,5-dimethylthiophene, and 2,5-diethylthiophene, and as a result the following compounds have been synthesized: 2-tert-butyl-5-methylthiophene, 2-tert-butyl-5-ethylthiophene, 3,5-di-tert-butyl-2-methylthiophene, 3,5-di-tert-butyl-2-ethylthiophene, 3-tert-butyl-2,5-dimethylthiophene, and 3-tert-butyl-2,5-diethylthiophene. The alkyl-substituted thiophenes were obtained in 85-95% yields.

2. The structures of these new tert-butyl-substituted thiophenes have been proved by acetylation in presence of stannic chloride.

3. It has been shown for the first time that, in the acetylation in presence of stannic chloride of trisubstituted thiophenes containing a tert-butyl group, the latter is eliminated when it occurs in the β-position.

4. 5-tert-Butyl-2-methyl-3-thienyl methyl ketone and 5-tert-butyl-2-ethyl-3-thienyl methyl ketone have been synthesized.

Received December 31, 1953

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CURRENT EVENTS

CONFERENCE ON THE THEORY OF THE STRUCTURE OF GLASS

From November 23 to 27, 1953, a conference was held in Leningrad on the theory of the structure of glass; it was convened conjointly by the Institute of Silicate Chemistry of the USSR Academy of Sciences, the All-Union Scientific Engineering and Technical Society of the Silicate Industry, and the S. I. Vavilov State Optical Institute of the Order of Lenin.

More than five hundred people took part in the conference; they represented about a hundred organizations (research institutes, higher-education establishments, industrial concerns, and ministries), and had traveled from twenty-eight cities.

Thirteen papers were read, and there were seventeen short speeches. About fifty people joined in the discussions.

After a short introductory address by Academician A. A. Lebedev, Prof. K. S. Evstropyev read a paper on the "Crystallite Theory of the Structure of Glass", in which he showed that since 1921, when the theory was propounded by Prof. A. A. Lebedev, many facts had been established that confirmed the presence in glass of ordered regions (crystallites), a phenomenon that is compatible with the phase diagrams of the systems studied. At the same time, during the intervening years, the crystallite theory has been developed and improved as our knowledge of the various properties of glass has extended. The present views on the structure of glass are formed by an integration of the theories of amorphous or network structure with the principles relating to crystallite formations. The modern crystallite hypothesis regards glass as a complex system, in which both crystalline and amorphous elements exist side by side, and it is of great importance to determine the relative volumes occupied in this structure by the ordered and amorphous parts.

In a paper by Corr. Memb. Acad. Sci. USSR P. P. Kobeko, entitled "Structure and Properties of Organic Glasses", it was shown that, on the basis of the classical studies of A. A. Lebedev and A. I. Strozharov, it must be considered that equilibrium amorphous structures must exist in a substance at below its melting point.

In his paper on the "Structure of Glass", Prof. O. K. Botvinkin suggested that the main structural elements characteristic of glasses were molecular groupings formed during the gradual cooling of the melt.

V. P. Barzakovsky Doc. Chem. Sci., who discussed D. I. Mendeleev's paper "Composition of Silica Compounds" as giving the first scientific theory of the structure of silicates, cited much recently discovered archive material, which showed that already in 1856 D. I. Mendeleev had built up an original chemical theory of the structure of silicates, differing essentially from the views of his predecessors and deeply penetrating into the essential nature of compounds of silicic acid. At the same time, Mendeleev suggested polymeric structures for silica and silicates.

Prof. V. V. Tarasov, in his paper on the "Quantum Theory of Specific Heats and the Structure of Silicate Glasses", gave an account of the results of his investigations on the quantum theory of the specific heats of chain and layer structures. The method developed by the author enabled determinations to be made of the vibration of the silicon-oxygen skeleton taken as a whole, and enabled conclusions to be reached concerning the architecture of the skeleton.

In her paper on "Concepts of the Internal Structure of Glasses Arising from the Results of an Investigation of Certain Properties of the Glasses of Simple Systems", L. I. Demkina Doc. Tech. Sci. showed that, when hyperbolic curves are transformed into straight lines on "composition-property" diagrams, and particularly on the "property-property" diagrams presented by the lecturer, discrete changes in properties may be detected, and these occur at compositions lying between definite chemical compounds and near to the eutectic points.

In a paper by Professors O. A. Esin and P.V. Geld, many facts were presented that indicated the energetic nonequivalence of ions in silicate melts and the microheterogeneity associated with this. These systems, in the authors' opinion, consist entirely of ions of various degrees of complexity. It may be supposed that glasses also consist of heteropolar formations, i.e. their structural elements are ions.

A. A. Appen Cand. Chem. Sci., in his paper on the "Coordination Principle of Arrangement of Ions in Silicate Glasses", showed that the properties of glass were determined not only by its composition, but also by its structure. The main structural factors that greatly affect the properties of glass are the degree of binding in the silicon-oxygen skeleton and the coordination state of the cations.

In his paper on the "Structure of Glass According to the Results of Investigations on the Structure of Porous Glasses and Films", S. P. Zhdanov Cand. Chem. Sci. discussed the results of investigations on porous glasses obtained by the leaching of sodium borosilicate glasses. The mechanism by which the formation of porous glasses is found to occur indicates that the original glass is on the whole heterogeneous in composition. The dimensions of these heterogeneous regions vary from tens to hundreds of Angstroms.

In their paper on "Raman Scattering and the Structure of Vitreous Substances", Corr. Memb. Acad. Sci. USSR E. F. Gross and V. A. Kolesova stated that the spectrum of inorganic glasses having low softening points (the system KNO_3–$NaNO_3$–$Ca(NO_3)_2$ and pyrophosphoric acid) does not change essentially when the substance passes from the liquid to the vitreous state, which is an indication of the similarity in structure of the substance in these two states.

In a study of two-component silicate glasses of the systems Na_2O–SiO_2 and K_2O–SiO_2, it was shown that the spectrum of the glass changes in regular fashion as the alkali content of the glass is increased. Hence, spectroscopic methods for the investigation of glasses have as yet given no proofs of the existence of crystallites in glass.

V. A. Florinskaya Cand. Phys. Math. Sci. and R. S. Pechenkina in a paper on the "Spectra of Simple Glasses in the Infrared Region, and Their Relation to the Structure of Glass" communicated the results of a comparison of the infrared spectra of original and devitrified glasses; broadening of the bands in the spectra on passing from devitrified to homogeneous glass indicates, in the authors' opinion, that in the latter there exist groups of atoms having an ordered array, similar to the array found in the lattice of the corresponding silicate.

In his paper on the "Possibilities and Results of X-Ray Methods of Investigating Vitreous Substances", E.A. Porai-Koshits Cand. Phys. Math. Sci. showed that the X-ray analysis of simple (one-component) glasses proved beyond doubt that large regions of inhomogeneity having dimensions of greater than 15-20 A were absent. E.A. Porai-Koshits discussed also the results of a study of the products of leaching sodium borosilicate glasses by the method of X-ray scattering at very low angles. These results enabled the regions of heterogeneity in the original glasses to be determined.

A. I. Stozharov Cand. Phys. Math. Sci., in his paper on the "Thermal Expansion of Glasses in its Relation to the Question of the Structure of Glass", gave the results of a careful study of the thermal expansion curves of glasses, on which breaks could be detected that could be ascribed to definite components of the glasses.

Active Memb. Acad. Sci. Byelo Russian SSR A.N. Sevchenko, in his paper on the "Use of the Luminescence Method for the Study of the Vitreous State", showed, on the basis of experiments on uranyl glasses, that this method permits the investigation of the immediate surroundings of the centers of luminescence, i.e. the super-fine structure. The experimental results of an investigation of quenching and of luminescence spectra at various stages of quenching for uranyl glasses show that the vitreous state should be regarded as a dispersion of finely crystalline formations (crystallites) in an amorphous pseudo-solution of glass.

V. A. Ioffe Cand. Phys. Math. Sci. gave an account of the results of his investigations on the dielectric losses in simple glasses (alkali and lead binary systems) at low temperatures and at high and super-high frequencies.

In his paper on the "Rayleigh Scattering of Optical Glasses, and the Structure of Glass", D.I. Levin, Cand. Phys. Math. Sci., showed that molecular (Rayleigh) scattering is the result of heterogeneity in the actual structure of the optical and sodium borosilicate glasses investigated, and is not due to "frozen-in" deformation and strains.

S.K. Dubrovo Cand. Chem. Sci., in his paper on the "Instability of Vitreous Silicates and Aluminosilicates toward Aqueous Solutions, and its Relation to the State of Silica in Glass", associated the chemical stability of glass with its crystallochemical characteristics, showing that the passage of Na_2O, Al_2O_3, and SiO_2 into solution in presence of acids is determined by the nature of the bonds in the aluminum-silicon-oxygen skeleton of the glass.

In her paper on the "Chemical Stability of Glasses of the Ternary System Sodium Oxide--Boric Anhydride Silica", O.S. Molchanova showed that the reactivity of these glasses toward aqueous solutions depends on the state of boron in the glass and the possibility of the formation of water-soluble compounds as a result of the reactions.

The formation of porous glass is a result of the hydration of silica, not only at the point of rupture of the O-Na bond, but also of the bonds of B-O-Si.

Papers by Yu. A. Gastev and A.F. Zak considered questions relating to the chemical stability of glass. New data concerning the properties of complex glasses were communicated by Prof. M.M. Gurevich, A.G. Repa, G. A. Stepanov, and L.A. Afanasyev. A detailed exposition of the works of D.I. Mendeleev was given by L.G. Melnichenko in his paper on the "Theoretical Views of D.I. Mendeleev on the Structure of Silicates and Glass, and Their Significance for Modern Science".

In the discussions that followed descriptions were given of new experimental investigations, and the fundamental problems of the structure of glass, already portrayed by the lecturers, were discussed in particular detail.

Prof. A. I. Avgustinik referred to investigations on the micro-hardness and reflection spectra of glasses obtained by the fusion of feldspar with various additions. It was found that the micro-hardness of a fire-polished surface of glass was considerably different (generally higher) than that of glass after grinding and polishing with rouge, which is explained by the author by the formation of crystallites of stable chemical composition suitably oriented at the surface. The reflection spectrum of glasses of enhanced micro-hardness contains a line corresponding to the linkage Si-O-Al. D. I. Dobychin, Cand. Chem. Sci., considered, on the basis of his investigations, that, when opalescent glasses of the $Na_2O-B_2O_3-SiO_2$ system are leached with acid, no secondary silicic acid is formed in the pores.

N. K. Voskresenskaya, Doc. Chem. Sci., has shown that many of the salt combinations that she has studied form melts in which a "tendency to form layers" is observed, which indicates the existence of micro-regions in the melts that differ among themselves greatly in composition. A similar micro-heterogeneity must remain in supercooled melts, and therefore also in glasses.

Prof. G.M. Bartenov demonstrated the incorrectness of both of the extreme points of view on the structure of glass: as a polycrystalline formation, and as a completely disordered network. The ordered regions, 15-20 A in size, assumed to exist in simple glasses cannot serve as nuclei for a new phase and are regions of close order without defined limits.

Academician N.V. Belov pointed out that the structural unit of a silicate glass, as established by X-ray analysis, is the SiO_4 tetrahedron, but the methods of X-ray analysis are not able to give a more detailed picture of the arrangement of atoms in glass. In order to speak of crystallites, these must contain about 10,000 elementary cells; only then can the X-ray methods give any indications concerning their structure.

N.V. Belov considered that the basic idea of Zachariasen concerning the presence of a disordered silicon-oxygen network in glass is correct. It is, however, necessary, as A.A. Appen has done, to take into account the possibility of differentiation, resulting in the formation of regions corresponding in composition to definite chemical compounds. In the solidification of melts, there is a continuous piling up of SiO_4 tetrahedrons, forming defined "fragments" of anionic radicals.

In N.V. Belov's opinion, there is no need to assume that spaces (vacuoles) filled with borates exist in borosilicate glass. In the cooling of a borosilicate glass, a considerable proportion of the BO_4 tetrahedra are converted into triangles. As a result, weak places are formed that are susceptible to the action of water or acids.

Modern crystal chemistry, stated Prof. G.B. Boky, has established that molecules do not exist in silicates, so that to assume the existence of molecular groupings in glass, as Prof. O.K. Botvinkin does, is incorrect. In glass there are ordered regions. It does not follow from this, however, that we must reject Zachariasen's hypothesis and confine our attentions to the crystallite theory of the structure of glass. There are no unreconcilable contradictions between the crystallite and continuous-network theories. In glass there are ordered and less ordered regions between which there are continuous transitions, and there are no phase boundaries. This viewpoint, which is a synthesis of the two theories, must be placed at the basis of concepts concerning the structure of glass.

Prof. V. Ya. Anosov pointed out that geometric transformations of diagrams, such as those made by L.L. Demkina, must always be subjected to mathematical analysis, since otherwise particular characteristics may disappear from or appear in the curves and lead to incorrect interpretation. Prof. Anosov considered that it is impossible to speak of a discrete point on curves expressing the properties of glass; it is better to use the term "break" or "singular point". Prof. Anosov also warned against the incorrect concept of a liquid as a chaotic

assembly of molecules.

V.S. Molchanov considered that those defending the primitive crystallite theory are insufficiently acquainted with the history of the question. In fact, the author of the crystallite theory, Academician A.A. Lebedev, stated in 1940 that between the continuous-network and crystallite theories "there is strictly speaking no essential difference; there is only a quantitative difference". The history of the conflict between the crystallite and Zachariasen hypotheses and of their development is similar to that of the conflict between the corpuscular and wave theories of light; it is an example of the conflict of contradictions and of the higher synthesis of these contradictions.

Prof. G.I. Skanavi considered that the vehement discussion at the conference did not derive from the apparently opposed positions ("crystallite" and "network") taken by the disputants, but was concerned rather with the fact that some were talking about the macroscopic properties of the system (viscosity, crystallization, thermodynamic stability), and others were trying to propose methods that would reveal the microstructure of glass although there are still no unequivocal experimental methods for the determination of structure of the close-order regions in glass. In G.I. Skanavi's opinion, the most hopeful direction of work in this field is the study of dielectric losses, which are most closely associated with the details of the structure of glass.

Active Memb. Acad. Sci. Byelo Russian SSR M.A. Bezborodov, referring to the great significance of the work of Academician A.A. Lebedev, pointed out that the crystallite hypothesis of A.A. Lebedev had infused new blood into the science of the vitreous state of matter. It constituted daring scientific innovation, and it demanded a fundamental review of obsolete concepts concerning the structure of glass. It determined also the further course of investigations on vitreous substances both here and abroad.

Prof. N.A. Toropov considered that the main problem confronting the investigators of glass was the determination of the relative dispositions and coordinates of the separate material particles. This difficult problem is not a hopeless one, and a time will come when we shall have as clear a concept of the structure of glass as we have of the structure of crystals. The investigation of the extremely fine mechanism of the formation of a larger ordered region - a crystalline nucleus in glass - forms one of the ways of solving the problem of the vitreous state. Great significance for the understanding of the vitreous state is associated with the study of the solid solutions and crystalline phases of variable composition that are often observed in complex silicate systems.

Workers on the structure of silicate glasses must keep in close touch with the investigators of organic glasses. From what may sometimes appear to be conflicting concepts, a more correct picture, reflecting the full complexity of the substances studied, may develop.

Other participants in the discussion were Prof. N.V. Solomin, Prof. K.G. Kumanin, Prof. I.F. Ponomarev, Prof. A.G. Bergman, and Candidates of Science V.A. Presnov, G.O. Bardykyants, V.T. Slavyansky, L.V. Sergeev, Yu. N. Andreev, B.I. Markin, V.P. Pryanishnikov, and others.

Summing up the conference, Academician A.A. Lebedev stated that as a result of the lively discussion the question of the structure of glass had been considerably clarified, and common points of view had been established. Everyone now agreed that there are ordered and disordered regions in glass, and whether we should call them crystallites or regions of close order or a network having an ordered arrangement of lattice points - this is a terminological question. We may consider that at the present time our picture of the structure of glass is fairly clear from the qualitative point of view. It is now necessary to pass to the next stage of the study of vitreous substances - to the quantitative side of the question. For example, we do not yet know the dimensions of the ordered and disordered regions in glass.

We can arrive at an understanding of the structure of glass only as a result of the application of numerous fine methods of investigation, and only when the results of many methods agree can we make reliable inferences.

In the resolution that was passed concerning the "Present State and Ways of Further Development of the Theory of the Structure of Glass", it is stated "that the development of the crystallite hypothesis and the hypothesis of close order has now resulted in a unified point of view on the question of spatial order in the arrangement of atoms in glasses (which indicates the presence of chemical bonds)".

"The Conference considers that one of the main problems is the creation of a general theory of the structure of vitreous substances, which would explain, not only qualitatively, but also quantitatively, the main characteristic features of structure present in glasses of all types, i.e. vitreous forms of elements and one-component and complex inorganic and organic glasses.

"The Conference considers that it is of extreme importance to seek and develop a method that would permit the establishment of the spatial disposition of the atoms, ions, and molecules in glasses with the same degree of probability as this can be done by X-ray analysis for crystalline substances."

A large section of the resolution was devoted to the enumeration of concrete problems confronting the research organizations working on vitreous substances. Thus it is proposed to intensify or renew work on X-ray, electron, and neutron diffraction investigations of the structure of glasses, on electron microscope and ultrasonic investigations, on infrared, ultraviolet, and Raman spectra, on luminescence and Rayleigh scattering, on the variation over a wide temperature range of optical, electrical, mechanical, and other properties of glasses, on the application of the method of labeled atoms, of the quantum theory of specific heats, of methods of physicochemical analysis, and so on.

It was considered that another important problem is the establishment of an agreed terminology for the description of the structure of glasses, and the Institute of Silicate Chemistry of the USSR Academy of Sciences was allotted the task of developing a new terminology project.

The Conference considered that it was very unsatisfactory that many authors should treat their experimental results in an excessively biased way - from the point of view of a single one of the existing hypotheses on structure - and it expressed the hope that, in newly published literature (including textbooks), an objective and critical treatment would be given of the present state of the theory of the structure of glasses and of the historical development of the various hypotheses.

The resolution concluded by pointing out the need to intensify work on the philosophical generalization of the concrete experimental material relating to questions concerning the structure of glass, and the need also to develop the historical side of the chemistry and technology of glass in our country, emphasizing particularly the significance of the works of Lomonosov and Mendeleev.

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SOME REGULARITIES OF THE CHANGE OF CATHODIC POLARIZATION DURING DEPOSITION OF METALS IN PRESENCE OF SURFACE-ACTIVE ADDITIVES

Yu. Yu. Matulis and A. I. Bodnevas

The employment of colloidal and surface-active additives in electroplating has been practiced for nearly fifty years. As early as 1905, Senn[1] observed that the addition of glue or gelatin to solutions for electrolytic lead plating appreciably improves the uniformity and smoothness of the lead deposits at the cathode. Sieverts and Wippelmann [2] in 1912 carried out some experiments to clarify the reaction of colloids with metallic deposits at the cathode. Izgaryshev and co-workers [3-5] were the first to study the influence of surface-active agents on polarization during discharge of metallic ions and established a series of characteristic features of this phenomenon, thereby starting the systematic study of the effects of colloidal and surface-active agents on electrode processes and the structure of the electrolytic deposit.

At the present time certain colloids and surface-active agents are widely employed in electroplating practice and their action has been widely studied in many investigations. Among these we may mention in particular the work of Loshkarev and co-workers [6-9], Vagramyan [10], and Frumkin and his school [11-15]. In spite of the numerous researches in the field of the action of surface-active agents on cathodic polarization and the quality of the electrodeposits, there are still many unsolved theoretical and practical problems. To take but one example, due to the absence of rules, the selection and application of various organic and colloidal additives in solutions of electrolytes during electroplating of metals has been made on a purely empirical basis. Consequently further study of this problem, especially in association with the discovery of new methods of investigation, is fully justified and desirable.

Our present research is a first attempt to determine the velocity and magnitude of the change in cathodic polarization under the action of surface-active agents in dependence on their chemical composition and molecular structure. The additives selected for this study were the simplest aliphatic alcohols from methyl through amyl, and the mono- and dicarboxylic acids: formic, acetic, propionic, butyric, valeric, oxalic, malonic and succinic; their effect on the cathodic polarization of copper, silver, nickel and zinc was studied.

EXPERIMENTAL

Method of investigation. Experiments on electrolysis and changes of polarization were conducted in a rectangular cubic vessel with a capacity of 130 ml. To opposite sides of the vessel were attached (with pure paraffin wax) electrodes with a total active surface of 2cm each. The anodes were plates prepared from analytically pure metals while the cathodes were sheet platinum densely coated with an electrodeposit of the metal under test. For the determination of changes of cathodic polarization, the auxiliary electrodes were of the same metals deposited electrolytically on platinum in the conditions used for preparation of the cathodes. Consequently, the electrolysis vessel, the intermediate vessel and the auxiliary electrode contained the same solution with ions of the investigated metal and, in the absence of a polarization current, the potential difference between the investigated cathode and the auxiliary electrode was practically zero. This eliminated the influence on the potential of trace amounts of any substances introduced with the reagents and permitted accurate determination of the change of potential of the cathode under the action of additives only introduced with the electrolyte subjected to examination.

The set of vessels with electrodes was placed in a thermostat in which the temperature was held at 25 ± 0.1°. The electrolyte in the electrolytic cell was stirred with a mechanical stirrer at a constant rate of 200 r.p.m. In the experiments with copper an electrolyte was used which consisted of 0.1 N $CuSO_4$ solution and 0.1 N H_2SO_4. Experiments with zinc were conducted in 1N $ZnSO_4$ solution; with nickel in 1N $NiCl_2$ with silver in 0.5 N $AgNO_3$ solution. All the substances were used in the analytically pure grades and were further purified by recrystallization (by distillation if liquid).

Measurements of the velocity and magnitude of changes of polarization potential. Measurements of the rapid changes of the potential of deposition of ions of the investigated metal on introduction of the additives into the electrolyte were performed by the compensation-oscillographic method. The principle of the apparatus developed and of the connecting-up of the 3-loop mechanical oscillograph in the general measuring scheme are represented in Figure 1.

In the latter, P is the electrolysis cell; C is the auxiliary electrode; Y is the three-lamp amplifier; T_1T_5 are the loops of the mechanical oscillograph; Ak_1, Ak_2, Ak_3 are accumulators; E_0 is an electromagnetic break with the frequency of oscillation of alternating mains current, i.e. 50 periods sec.

Since the change of cathodic polarization could be increased by the amplifier Y by several powers of ten up to $(25)^3$ times, before each experiment after establishment of a constant heating and a specific anodic voltage of the cathode tubes in the amplifier, calibration was carried out of the oscillograph recordings. Use was made for this purpose of a potentiometer B consisting of a resistance box R_4 inserted in the circuit of the amplifier and the oscillograph, by means of the switch n. By giving definite potentials at the terminals of the amplifier Y, the amplitude was noted of the light traces on the drum of the oscillograph and the corresponding curve was plotted and then served for evaluation of the changes of cathodic potential in the electrolysis cell P. After the oscillographic traces had been calibrated, the switch n was shifted to contact a so that the amplifier Y and the oscillograph were connected into the measuring circuit and the variable resistance R_6 was used to establish a determined current density at cathode K. Then, after compensation of the difference of potentials between cathode K (being polarized) and the auxiliary electrode, the potentiometer A was used to introduce into the electrolysis cell P an exactly predetermined amount of surface-active additive and the change of cathodic potential was recorded on the oscillograph drum. Consequently our method of measurement permitted precise determination of the rise or fall of cathodic polarization, depending exclusively on the action of the introduced additives at any desired current density, and also enabled the change of this potential to be followed in the course of any desired interval of time.

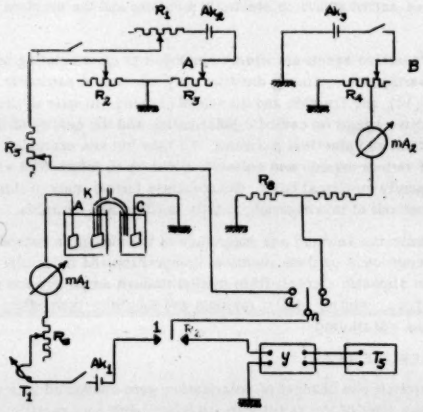

Fig. 1. Set-up of compensated oscillographic apparatus for measurement of magnitude and velocity of change of polarization.

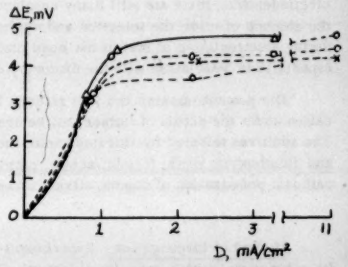

Fig. 2. Dependence of shift of cathodic potential of copper, on addition to the electrolyte of organic acids, on the current density: o – 25,16 mM/l CH_3COOH; x – 6,26 mM/l CH_3CH_2COOH; • – 5,8 mM/l $CH_3CH_2CH_2COOH$; △ – 2,6 mM/l $CH_3CH_2CH_2CH_2COOH$

EXPERIMENTAL RESULTS AND THEIR EVALUATION

The change of cathodic potential under the action of surface-active admixtures depends up to a certain degree on their amount, on their chemical composition and on the current density. This dependence is illustrated in Figures 2 to 4. In Figure 2 are plotted data which show the increase of cathodic polarization when copper is precipitated as the result of introduction into the electrolyte of definite amounts of acetic, propionic, butyric and valeric acids at various current densities, the amounts of introduced acids being so selected that the deposition potential of the copper ions increased approximately by the same amount. As we see from Figure 2, with unchanged concentration of additives, the shift of cathodic potential remains substantially constant and does not change with further rise of current density. The form of the curves is identical for all the additives studied. It may be noted that, in the present case, valeric acid is roughly 9.5 times as active as acetic acid. Propionic and butyric acids take up an intermediate position in respect of activity.

With increase of concentration of the same acids as additives with unchanged current density, the change of the cathodic potential of copper follows a curve similar to an adsorption isotherm. These curves, which were plotted for acetic and propionic acids at a current density of 0.71 mA cm^2 are shown in Figure 3. Side by side with them are given the curves 3 and 4 which were plotted for the same acids at a current density of 7.1 mA cm^2. A comparison of curves 1 and 3 and of 2 and 4 clearly shows that the very same amount of acetic or propionic acid, introduced as additive, brings about a shift of cathodic potential of copper which is the greater the higher the current density at the cathode. Consequently, with increasing current density, the adsorption of those acids at the surface of the cathode increases. This phenomenon was also observed in the case of butyric, valeric, oxalic, malonic and succinic acids on copper cathodes; in all probability it depends on the increase in the actual surface of the cathode and on the growth thereon of a number of active centres when stronger currents are passed through.

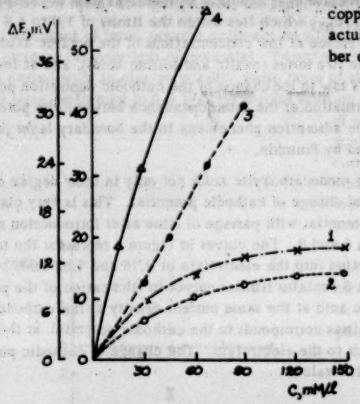

Fig. 3. Magnitude of change of potential of copper deposition as a function of the amount of acetic and propionic acids introduced as additives into an acidified solution of copper sulfate: 1- with addition of acetic acid; 2- with addition of propionic acid at a current density of 0.71 mA /cm^2; curves 3 and 4 are similar curves obtained at a current density of 7.1 mA/ cm^2.

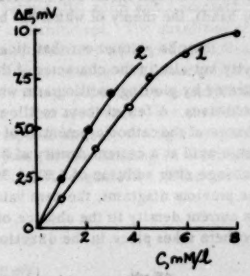

Fig. 4. Magnitude of change of deposition potential of copper as a function of the amount of malonic and butyric acids introduced into the electrolyte as additives, at a current density of 3.7 mA /cm^2: 1- with addition of malonic acid; 2- with addition of succinic acid.

As already remarked, on introduction of fatty acids as additives, the jump in cathodic potential ΔE at constant current density increases with the rise in the number of carbon atoms in the homologous series. This is directly apparent when we examine the curves in Figs. 2-4. The plots in Fig. 4 show the change in cathodic potential as a function of the concentration of the added dicarboxylic acids – malonic (1) and succinic (2) – at a constant current density of 3.7 mA /cm^2. We see from Fig. 4 that the activity of the additives is not only a function of the number of carbon atoms in the homologous series but is also markedly dependent on the number of polar groups in the molecule. This is also very clearly brought out by the data in the table which show the amounts of acetic, propionic, malonic and succinic acids in mM/l needed for raising the cathodic potential of copper ΔE by 2,4, and 5,5 mV with an unchanged current density of 3.7 mA/ cm^2.

TABLE

Amounts of Acids Needed to Change the Potential of Copper by 2, 4, and 5,5 mV.

Δ in mV	Concentration of acids in mM / liter			
	acetic	propionic	malonic	succinic
−2	15	2,6	1,2	0,8
−4	35	8,0	2,4	1,5
−5,5	50	13 ,0	3,3	2,25

An examination of the numerical data in the table, as well as in Figs. 3 and 4, immediately shows that for the attainment of a uniform effect, i.e. a rise in cathodic polarization by the same amount along the rising portion of curve E — C, the organic acids are arranged in a strictly defined order; the longer the chain of a homolog, the lower is its concentration which promotes an identical cathodic overvoltage. Furthermore, the dicarboxylic acids are roughly 3.5 to 15 times as active as the monocarboxylic acids with the same number of carbon atoms in the molecule. Consequently, the presence of an additional carboxylic acid group in the acid molecule considerably increases its surface activity in the conditions here considered. Comparing the concentration for one member of the homologous series c_n with the concentration of the next member c_{n+1}, causing an identical shift of cathodic potential at an identical current density, we obtain the ratio c_n / c_{n+1} which lies within the limits of 1.8 to 5.8 for monocarboxylic acids and 1.50 to 1.75 for dicarboxylic acids. Hence at low concentrations of the organic acids used as additives, with the exception of the first members of the two series (oxalic and formic acids), and at low current densities, we find approximate applicability of Traube's law to the change of the cathodic deposition potential of copper ions from acid solutions. This is one more confirmation of the interdependence between the potential difference between metal and solution (on the one hand) and the adsorption phenomena in the boundary layer (on the other hand), the theory of which has been successfully developed by Frumkin.

It must be pointed out that dicarboxylic acids differ from monocarboxylic acids not only in their degree of activity but also in the character of their action upon the rate of change of cathodic potential. This is very clearly illustrated by plotting oscillograms which show the change of potential with passage of time after introduction of the additives. A few of these oscillograms are shown in Figures 5 and 6. The curves in Figure 5 represent the rate of change of the cathodic potential of copper ΔE after introduction into the electrolyte of 3.76 and 7.52 mM/l of malonic acid at a current density of 3.7 mA/cm², while Figure 6 contains similar curves in illustration of the potential change after addition of 0.81, 1.64 and 3.29 mM/l succinic acid at the same current density at the cathode; as in the previous diagrams, the zero value on the axis of the abscissas corresponds to the cathodic potential at the given current density in the absence of additions of organic acids to the electrolyte. The change of cathodic potential everywhere takes place in the direction of increase of its negative value.

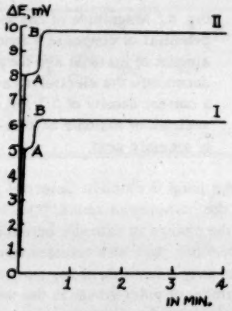

Fig. 5 Rate of change of deposition potential of copper after introduction into the electrolyte of malonic acid at a cathodic current density of 3.7 mA/cm²; I - 3.76 mM/l; II - 7.52 mM/l.

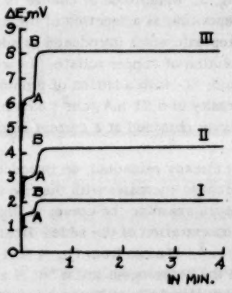

Fig. 6. Rate of change of deposition potential of copper after introduction into the electrolyte of succinic acid at a current density of 3.7 mA/cm²: I - 0.81 mM/l; II - 1.64 mM/l; III - 3.29 mM/l.

As we see from these diagrams, within only a minute after introduction into the electrolyte of the dicarboxylic acids, with stirring of the electrolyte at a speed of 200 r.p.m., two jumps of cathodic potential occur in rapid succession. The height of these jumps depends on the amount of acid added. The higher the concentration of malonic or succinic acid in the electrolyte at the given current density, the higher the initial potential jump A and the greater the distance AB between the two jumps. It should be noted that with monocarboxylic acids, two analogous jumps are not observed. After the first jump the ΔE versus time plot abruptly bends over and runs the whole time parallel to the abscissas.

This new and interesting phenomenon, observed with dicarboxylic acids, clearly points to a definite interrelation between the change of cathodic polarization and the specific structure of the additives employed. At present it cannot be otherwise explained than by a type of adsorption peculiar to molecules containing two polar groups. It may be suggested that at the start the molecules of dicarboxylic acid adsorbed on the surface of the cathode are orientated with only one carboxyl group parallel to the surface. After a certain, fairly short, period of time, the molecules undergo rearrangement in the adsorbed film and the other carboxyl group becomes more firmly bonded to the surface of the metal. Due to this the same number of adsorbed molecules more completely fill the surface of the metal and brings about the second sharp potential jump at the cathode.

Additions of lower organic acids act on silver cathodes in exactly the same way as on copper cathodes, i.e. they increase the polarization potential. Experiments with silver cathodes were carried out using platinum electrodes coated with an electrolytically dense layer of silver deposited from cyanide solutions. Polarization measurements were performed in 0.5 N silver nitrate solution. In Figure 7 are shown the oscillograms for the rate of change of polarization when the electrolyte contains definite amounts of acetic (I), propionic (II) and butyric (III) acids and a constant current density of 3 mA/cm^2 is maintained. The quantities of acids added were so selected that approximately equal changes of cathodic potential were caused. The curves show that introduction of the additives brings about a sudden rise of polarization quickly followed by a fall to the original value. This penomenon, not observed in work with other metals, corresponds entirely to Vagramyan's observation of passivation of crystals of silver during its electrodeposition [16]. Once again it confirms his explanation of the causes of passivation.

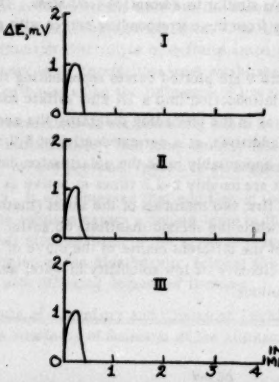

Fig. 7 Magnitude and velocity of change of precipitation potential of silver on addition of organic acids to the electrolyte: I - 12.72 mM/l acetic acid; II - 4.02 mM/l propionic acid; III - 1.5 mM/l butyric acid. Current density of 3.0 mA/cm^2

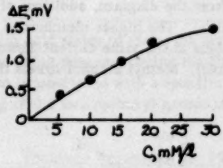

Fig. 8 Rise of original jump of the precipitation potential of silver with increase of concentration of the propionic acid added to the electrolyte at a cathodic current density of 1.43 mA/cm^2

From the curves of Fig. 7 it can readily be seen that the ratios of concentrations of acids causing the original jump of polarization potential by the same amount at constant current density is in accord, as in the case of copper, with Traube's law. Furthermore, the rise of the original potential change with increasing amounts of added acid at constant current density is represented by a curve similar to an adsorption isotherm. An example of this type of curve, plotted for propionic acid at a current density of 1.43 mA/cm^2, is presented in Figure 8.

The experiments described show that the nature of the action of the very same additives on the polarization of copper and silver cathodes is dissimilar. This difference is even more conspicuously manifested in the case of the cathodic polarization of zinc and nickel. Additions of lower organic acids to 1 N solution of zinc sulfate and 1N solution of nickel chloride do not raise the cathodic polarizations of zinc and nickel but considerably lower them. The polarization during cathodic precipitation of zinc is lowered to a relatively greater extent by the higher members of the homologous series of acids. For example, at low cathodic current densities, the addition of butyric acid lowers the polarization during precipitation of zinc about twice as much as on addition of the same amount of acetic acid. It should be noted that the introduction of lower organic acids into zinc sulfate solution appreciably lowers the pH of the electrolyte and much hydrogen begins to be evolved at the cathode at the same time as the zinc is

deposited. The concomitant evolution of hydrogen and the relatively small effects of the potential change preclude the possibility of precise determination of any quantitiative regularities similar to those established for copper and silver cathodes.

The hydrogen evolution accompanying the main process still more conceals the general picture of the phenomena when working with nickel cathodes. On nickel cathodes it was impossible to establish any specific action of the added acids. Each acid lowers the cathodic polarizaton of nickel approximately in proportion to the fall in pH of the solution. For example, additions of hydrochloric acid and propionic acid to 1N nickel chloride solution reduce the polarization of nickel by approximately the same amount if the pH of the electrolytes are brought to identical values.

In order to avoid the complications resulting from evolution of hydrogen at zinc and nickel cathodes when using lower acids as additives, experiments were carried out with additions of lower alcohols of the aliphatic series. It was found that methyl, ethyl, propyl, butyl and amyl alcohols do not manifest any action on the polarization during precipitation of silver and nickel at any current densities. Their effect on the polarization of copper cathodes is in the same direction as that of the organic acids, i.e. they render the deposition potential of copper more negative. Although the potential shift of copper on addition of alcohols to the solution is less than on addition of acids, the same regularities of change of polarization could be observed except in the case of methyl alcohol, as were found with acids, namely, the applicability of Traube's law and the possibility of representation of the potential change as a function of the concentration of additives at low current densities by curves similar to adsorption isotherms. The curves for copper cathodes obtained with alcohols do not differ essentially from the corresponding curves with acids and are therefore not reproduced here.

The results obtained with zinc are very similar in character. In Figure 9 are plotted curves representing the magnitude and velocity of change of the cathodic potential of zinc after introduction into a 1N zinc sulfate solution of 65 mM/l of the alcohols mentioned at constant current density. Here, as in the preceding diagrams, the zero line denotes the polarization potential of zinc in pure $ZnSO_4$ solution without additives, at a current density of 5.7 mA/cm^2. As we see from the diagram, additions of propyl, butyl and amyl alcohols appreciably raise the polarization during zinc deposition. The higher members of the homologous series of alcohols are roughly 2-2.5 times as active as the lower members at the same current density. An exception arises with the first two members of the series (methyl and ethyl alcohols). Methyl alcohol lowers the polarization by about 0.5 mV while the second manifests no action at all. The cause of the different course of the curve of amyl alcohol is evidently its low solubility in water and aqueous solutions.

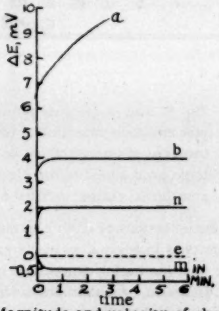

Fig. 9. Magnitude and velocity of change of deposition potential of zinc after introduction into the electrolyte of alcohols: m - 1N ZnSO + 65 mM/ 1 CH_3OH; e – 1N $ZnSO_4$ + 65 mM/1 CH_3CH_2OH; n - 1 N $ZnSO_4$ + + 65 mM/1 $CH_3CH_2CH_2OH$; b - 1 N $ZNSO_4$ + 65 mM/1 $CH_3CH_2CH_2CH_2OH$; a - 1 N $ZnSO_4$ + 65 mM/1 $CH_3CH_2CH_2CH_2CH_2OH$. Current density 5.7 mA/cm^2.

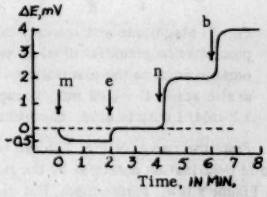

Fig. 10. Change of deposition potential of zinc on successive addition of alcohols to the same electrolyte: m – 65 mM /1 CH_3OH; e – 65 mM/1 CH_3OH + 65 mM /1 CH_3CH_2OH; n – 65 mM/1 CH_3OH + 65 mM/1 CH_3CH_2OH +65 mM/ 1 $CH_3CH_2CH_2OH$; b – 65 mM/1 CH_3OH + 65 mM /1 CH_3CH_2OH + 65 mM/1 $CH_3CH_2CH_2OH$ + 65 mM/1 $CH_3CH_2CH_2CH_2OH$.

It is interesting to note that successive introduction of one alcohol after another into the same portion of zinc sulfate solution leads to stepwise change of potential. Addition of a definite amount of a higher homolog of the alcohol series causes a potential change whose magnitude does not depend on the presence in the solution of a lower alcohol. This is illustrated by the plot in Figure 10; at point m 65 mM/liter methyl alcohol was added to the solution; after a period of 2 minutes addition was made to the solution of 65 mM/liter ethyl alcohol, followed after 4 minutes by 65 mM/liter propyl alcohol, and after a further 6 minutes by 65 mM/liter butyl alcohol. The current density throughout the whole of the experiment was kept constant at 5.7 mA/cm^2. This interesting phenomenon clearly indicates the displacement of an alcohol by the next highest homolog from the surface of the electrode, since the higher alcohols have a greater surface activity and are more firmly adsorbed at the surface of the metal.

SUMMARY

1. A compensation-oscillographic method has been developed for measuring the magnitude and velocity of polarization changes on introduction of various additives into an electrolyte during electrolysis. This method was used to investigate the influence of simple organic compounds (formic, acetic, propionic, butyric, oxalic, malonic and succinic acids and methyl, ethyl, n-propyl and n-butyl alcohols), introduced as additives, on the cathodic polarization during deposition of copper, silver, zinc and nickel within the current density range of 1 to 10 mA/cm^2.

2. It was established that the rise of cathodic polarization on precipitation of copper with rising concentration of the acids and alcohols added to the electrolyte at constant current density not exceeding 10 mA/cm^2 follows a curve similar to an adsorption isotherm. The absolute magnitudes of the shift of cathodic potential provoked by introduction into the electrolyte of definite amounts of acids and alcohols of the same homologous series obey Traube's law. The very same regularities were established for silver cathodes under the action of lower organic acids, and for zinc cathodes under the influence of lower primary alcohols with the exception of methyl and ethyl alcohols.

Admixtures of organic acids cause only a temporary change of potential during deposition of silver following their introduction. This jump quickly falls to zero in the first half minute after addition of the acid to the electrolyte, i.e. the potential reverts to its original value.

3. It was observed that addition of the first members of the dicarboxylic acid series to the acidified copper sulfate solution causes a double jump in the cathodic polarization of copper which proceeds during the first 10–15 seconds after addition of the acid. It is suggested that this new phenomenon is associated with a specific course of adsorption of the dicarboxylic acids at the metal surface, involving bonding of the two carboxyl groups to the surface with differing degrees of firmness.

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Received September 19, 1953

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THERMOCHEMISTRY AND STRUCTURE OF ATOMS

COMMUNICATION 7. INVESTIGATION OF THE CARBONATES OF THE SECOND (MAIN) GROUP OF THE MENDELEEV SYSTEM

A. F. Kapustinsky and M. S. Stakhanova

INTRODUCTION

Consideration was given in one of the preceding communications to the application of the rule of thermochemical logarithmicity [1] to oxalates of alkaline earth metals [2]. In the present paper we develop the investigation with reference to the carbonates of the same elements in view of the particular practical and theoretical importance of these compounds in metallurgy, in the chemistry of building materials and in geochemistry. This paper includes in part the results not only of calorimetric measurements but also of our earlier determinations (made with the help of other methods) of thermodynamic constants of the carbonates of beryllium [3] and strontium [4,5]. The critically carried out systematization of the experimental data enabled the thermodynamics of the above-mentioned carbonates to be summarized; it also permitted the constants obtained to be generalized in the light of the rule of thermochemical logarithmicity and allowed a number of conclusions about the properties of the carbonate ion to be drawn.

The thermodynamics of the alkaline earth carbonates has been dealt with by many investigators, but in the majority of cases the measurements are not sufficiently accurate so that not only do serious discrepancies arise in the same type of measurements but there are unexplained deviations between calorimetric and high-temperature determinations of thermodynamic constants. This is illustrated by the monograph (documented in detail) of Kelley and Anderson [6]. Since the publication of the latter work, no substantial changes have taken place in this field, which circumstance made it not only desirable but even necessary that the present investigation should be undertaken.

EXPERIMENTAL

1. METHOD OF INVESTIGATION

Heats of formation were determined by studying the thermal effects of dissolution of finely crystalline (synthetic) $MgCO_3$ and $BaCO_3$ in 1 M solution of HCl at 25°. The hydrochloric acid was previously saturated with carbon dioxide at atmospheric pressure. The correction for evaporation of water was made as in the paper of Kapustinsky and Desideryeva [4]. In the case of $MgCO_3$ special attention was given to determination of the heat of solution of MgO in HCl.

The following changes were made in the calorimeter previously described by Kapustinsky and Klokman [7]. The thermostat was a Bose casing supplied with water from an adjacent thermostat with the aid of a water turbine. The temperature of the thermostat was maintained at 25 ± 0,005°. Current (120 V) was applied (Fig.1) to the heating spiral of the thermostat H_1 a vacuum relay VR was connected in series. The winding of the latter was connected to the tube (6F6) of an electrical relay whose heating circuit was supplied by the step-down transformer T, while the anode circuit was fed from the 120 V mains. Under normal emission the vacuum relay was switched in. On closing the contact of the thermoregulator TR (25°), however, the tube circuit was short-circuited, the amplification of the emission led to amplification of the current in the series winding of the vacuum relay, which breaks the contact in the main circuit and cuts out the heating spiral. The fall of temperature leads to closing of the circuit operating through the thermoregulator and consequently to resumption of heating. Since the current strength in the anode-mains circuit does not exceed $5 \cdot 10^{-4}$ A, there is no risk of burning-out of the contacts and of damage to the thermoregulator.

The calorimeter was a pyrex glass beaker, volume 0.45 l, closed with an ebonite stopper through which passed a Beckmann thermometer, a glass propeller stirrer, the leads of a Vrevsky mercury spiral, a glass tube with a bulb at the end containing a weighed amount of the substance, and a thin test tube for introduction (if needed) of freezing

mixture. The energy introduced for determination of the heat capacity of the solution was measured with the help of a potentiometric circuit which enabled alternate measurement of the voltage at the terminals of the divider and of standard resistance at definite intervals throughout the main period. The electrical measuring circuit (Fig. 2) consisted of a Rapp potentiometer II, a standard Weston element N, a 1-ohm standard resistance $R_{stand.}$, a resistance box r_1, r_2, and a mirror galvanometer G with a sensitivity of 10^{-9} A. In the diagram are also shown the calorimeter heater $R_{spir.}$, the loading resistances R_{load}, the rheostats R_1, R_2, the ammeter A, the switch and circuit switches k, k_1, k_2 and a battery of lead accumulators (6V). Current strength and voltage were measured to an accuracy of 0.0001 A and 0.0001 V for total effects of the order of 0.8 A and 0.5 V.

The temperature was measured with a Beckmann thermometer (calibrated against a standard instrument in VIMS) with the aid of a cathetometer to an accuracy of $\pm$ 0.001° for a rise of the order of 0.4°; the time was measured to an accuracy of 0.1 seconds for periods of 3 to 4 minutes. All the electrical measuring instruments were checked before the start of the work in the Weights and Measures Department and were provided with certificates. The stop watch was regulated against an accurate time signal; it was connected to the circuit by the usual switch scheme [8]. The operation of the apparatus and the introduction of corrections for radiation, also the mode of computation, are as described in the literature [7, 8, 9].

The apparatus was calibrated by an electrical method and against the heat of solution of potassium chloride. At the conclusion of an experiment, the temperature of the calorimeter was brought to the initial temperature and the water equivalent of the system was determined in conditions similar to those prevailing for determination of heats of solution. The accuracy of the determinations (heats of solution), allowing for the characteristics of the instrument that we used, the amounts of heat evolved and the weights of reagents, ranged from 0.6 to 1.6% (with MgO and $MgCO_3$) and to 3% (with $BaCO_3$).

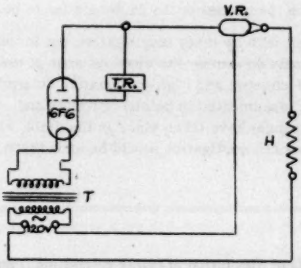

Fig. 1.

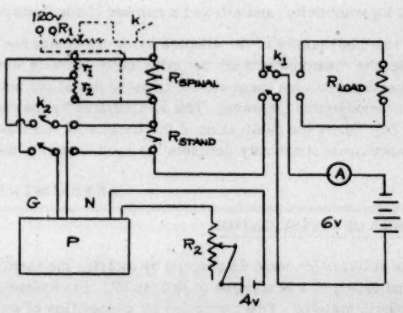

Fig. 2

A special place is occupied by the thermal investigation of beryllium carbonate which we described elsewhere [3] and the results of which are set forth in this paper. As is usual in investigations of dissociation equilibria, accurate allowance for all factors is impossible and moreover calorimetric measurements are impracticable, in this case. Nevertheless we consider it to be necessary to again draw attention to the arguments in support of the trustworthiness of our previous investigation: a) satisfactory maintenance of the linear dependence of log K on $1/T$; b) reproducibility of the results on approach to equilibrium both from the low- and the high-temperature side; c) non-dependence of the results on the degree of reduction of the weighed specimens (indicating absence of solid solutions); d) the crystallinity of the substances, confirmed both by microscopic and by X-ray examination (Fig. 3). The same may be said about the investigation of $SrCO_3$. An approximate evaluation in both cases gives an accuracy of determination of the heats of dissociation of 5 - 7%.

2. STARTING SUBSTANCES

a) Beryllium carbonate. We have already published a short account of the investigation of beryllium carbonate [3]. Here we limit ourselves to giving the X-ray diagram (Fig. 3) which testifies to the crystallinity of the material used.

Fig. 3.

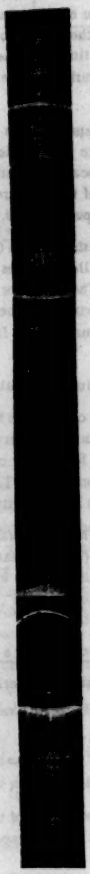

Fig. 4.

b) Magnesium carbonate. An attempt to utilize natural magnesite from the Satinsky deposit as starting material was unsuccessful because it is deficient in reactivity and even the purest specimens contain some pyrite.

Crystalline magnesium carbonate, free from basic salts, was prepared by two methods which gave identical results.

1) Solutions of chemically pure magnesium sulfate and chemically pure sodium carbonate were mixed at 80-100°. The resultant amorphous precipitate was washed several times on the filter with hot water, drained and dried. The dry precipitate was mixed with an equal volume of urea and heated for 2 hours at 140 - 145° in a porcelain crucible. Heating with urea converts the amorphous precipitate of basic salt into the crystalline form. The residues of hygroscopic water entered into reaction with the urea. On cooling, the caked mass was pulverized and repeatedly decanted to remove the urea and the turbidity due to non-crystallizing carbonate. After washing, the precipitate was dried at 100°.

2) The basic carbonate, again prepared from a boiling solution of magnesium sulfate and soda, was dried and then heated in a current of dry and pure carbon dioxide at 150° for 5 hours. After cooling in a carbon dioxide atmosphere, the carbonate was washed by decantation and then dried in the same apparatus in a CO_2 stream until constant in weight. The crystalline character of the prepared material was clearly confirmed both by microscopic and X-ray examination (Fig.4). Analysis gave a purity of 99.7%.

c) Magnesium oxide. The magnesium oxide (Kahlbaum) at our disposal was analyzed for its content of carbonate and moisture. Heating of two parallel samples at 1100° revealed the presence of 12.3% volatiles (carbonate decomposed by heating and moisture). Therefore for the thermochemical experiments we used the calcined oxide which, however, had not lost its reactivity. Magnesium was determined in the calcined sample by the pyrophosphate method. The results obtained (60.4% magnesium in MgO, theoretical value 60.3%) demonstrated the high purity of the starting material.

d) Strontium carbonate. Preparation and analysis have been described elsewhere [14].

e) Barium carbonate. Anhydrous, crystalline barium carbonate was obtained by reacting solutions of barium chloride and potassium carbonate (chem. pure recrystallized substances) at 80 - 100°. The precipitate was kept at the same temperature for several hours for growth of the crystals and washed on a porous glass filter. The wash liquors were tested for their content of chlorine ion. The washed precipitate was dried at 150 - 160°. Barium was determined as sulfate. The preparation had a purity of 99.6%.

f) Water and hydrochloric acid. The water was a double-distilled grade which we also used in the syntheses and in calorimetry. The hydrochloric acid (1M) was saturated with a slow stream of well-purified carbon dioxide which was passed through for 14-16 hours. Prior to each experiment the requisite amount of this acid was subjected to supplementary saturation with CO_2 (2-2½ hours) at 25°. The completeness of saturation was checked by titrating a small sample of the acid with caustic alkali solution.

3. Results of Calorimetric Determinations

In Table 1 are summarized the results of experiments with magnesium and barium carbonates.

The results obtained correspond to the reactions:

$$MgCO_{3(solid)} + 2HCl_{(1:55)} = MgCl_{2(1:2000)} + H_2O_{(liq.)} + CO_{2(gas)} + 12800 \pm 200 \text{ cal.} \quad (1)$$

$$BaCO_{3(solid)} + 2HCl_{(1:55)} = BaCl_{2(1:2000)} + H_2O_{(liq.)} + CO_{2(gas)} + 3370 \pm 110 \text{ cal.} \quad (2)$$

In order to calculate the heats of formation of the carbonates, we sum the heats of formation of the constituents of each system [13] with the effects that we observe:

$$\Delta H^\circ MgCO_{3(solid)} = \Delta H^\circ MgCl_{2(1:2000)} + \Delta H^\circ H_2O_{(liq.)} + \Delta H^\circ CO_{2(gas)} - 2\Delta H^\circ HCl_{(1:55)} - \Delta H,$$

$$\Delta H^\circ MgCO_{3(solid)} = -260{,}4 \text{ kcal/mole.} \quad (3)$$

$$\Delta H^\circ BaCO_{3(solid)} = \Delta H^\circ BaCl_{2(1:2000)} + \Delta H^\circ H_2O_{(liq.)} + \Delta H^\circ CO_{2(gas)} - 2\Delta H^\circ HCl_{(1:55)} - \Delta H,$$

$$\Delta H^\circ BaCO_{3(solid)} = -287{,}3 \text{ kcal/mole.} \quad (4)$$

From an inspection of the errors of determinations of the heats of formation of the reaction components, we may assume the limit of experimental accuracy of determinations of heats of formation of carbonates to be 0.3-0.4%, equivalent to a fluctuation of about one large calorie in the indicated magnitudes.

TABLE 1

Heats of Solution of Carbonates in 1 M HCl at 25° (with Correction for Evaporation of Water) in cal/mole.

Wt., in g	Wt. of H_2O, in g	Δt_1 (dissolution of carbonate)	Correction for radiation, in %	Δt_2 (determination of thermal equivalent of system)	Correction for radiation, in %	Thermal equivalent of system, in cal/degrees	Heat of solution, in cal/mole
			Magnesium Carbonate				
$MgCO_3$							
0,9640	400,10	0,344	1,25	0,351	1,3	422,5	12840
1,0290	400,00	0,370	2,1	0,386	6,9	415,8	12760
1,0240	400,09	0,370	6,0	0,350	4,1	418,6	12820
1,0265	400,38	0,356	3,4	0,318	0,8	427,8	12610
0,9445	400,25	0,341	3,3	0,240	5,0	425,4	13000
0,9498	400,00	0,340	1,6	0,338	0,5	418,3	12730
			Mean 12800 ± 200 cal (± 1,6%)				
			Barium Carbonate				
$BaCO_3$							
3,5041	400,51	0,144	3,3	0,358	3,4	413,6	3440
3,4822	400,85	0,136	0,51	0,463	1,46	415,7	3290
3,6378	400,62	0,151	0,86	0,197	0,3	414,3	3480
3,5013	400,72	0,144	0,4	0,194	0	414,0	3440
3,1980	399,25	0,128	1,9	0,101	5,3	402,4	3270
3,3650	401,35	0,133	0,7	0,218	0	419,7	3350
3,2591	400,99	0,128	1,6	0,279	0	417,7	3320
			Mean 3370 ± 110 cal (± 3%)				

One of the aims of the present investigation was the establishment of the heat of dissociation of carbonates into MeO and CO_2; this requires, apart from the data set forth above, a knowledge of either the heat of formation of the metallic oxide or the heat of its dissolution in HCl. Since among the materials that we investigated an especially important one for industry is $MgCO_3$, we undertook a determination of the heat of solution of MgO in hydrochloric acid in conditions close to those prevailing in the experiments on dissolution of $MgCO_3$. This leads to more accurate results because the summation of the heats of the two latter processes directly gives the heat of dissociation.

The weight of the sample of oxide was so selected that the concentration of magnesium chloride in solution corresponded to its concentration on dissolution of the carbonate (1:2000). The procedure for the calorimetric experiment in no way differed from that used above. The experimental results are set forth in Table 2.

Our experimental values agree within the limits of accuracy of our work (± 0,6%) with those of previous investigations of these materials by Giauque and Archibald [10] (36,490 cal/mole for the same dilutions). Mention may also be made of Alentyev's paper [11] which described a method of evaluation of natural carbonates.

From the known heat of the reaction

$$MgO_{(solid)} + 2HCl_{(1:88)} = MgCl_{2\ (1:2000)} + H_2O_{(liq.)} + 36320 \pm 230 \text{ cal.}, \quad (5)$$

we can obtain, by summation of this equation with equation (1), the heat of the reaction:

$$MgCO_{3\ (solid)} = MgO_{(solid)} + CO_{2(gas)} + 23520 \text{ cal.} \quad (6)$$

A similar calculation for the heat of dissociation of $BaCO_3$, taking into consideration the literature values for $\Delta H^\circ_{CO_2}$ and ΔH°_{BaO} [14] gives:

$$BaCO_{3\ (solid)} = BaO_{(solid)} + CO_{2\ (gas)} + 61000 \text{ cal.} \quad (7)$$

These constants are included in Table 3.

TABLE 2

Heat of Solution of Magnesium Oxide in 1 M HCl at 25°

Wt. of MgO, in g	Wt. of HCl, in g	Δt_1 (dissolution of oxide)	Correction for radiation, in %	Δt_2 (determination of thermal equivalent of system)	Correction for radiation, in %	Thermal equivalent of system, in cal/deg.	Heat of solution of MgO, in cal/mole
0,3814	401,15	0,812	1,03	0,778	4,9	422,8	36320
0,4029	400,02	0,861	0,36	0,799	1,17	422,5	36410
0,3920	400,07	0,847	2,8	0,754	5,6	419,7	36560
0,3880	400,06	0,828	0,24	0,769	2,3	420,6	36190
0,4027	403,51	0,884	1,5	0,808	3,8	427,6	36140
			Mean 36320 ± 230 cal (± 0,6)				

TABLE 3

Heats of Formation ($-\Delta H^\circ_{298}$) and Dissociation (q) of Carbonates of the Second Group at 25° in kcal

(A) $Me_{(solid)} + C_{(graphite)} + {}^3/_2 O_{2(gas)} = MeCO_3$ (solid)

Carbonate	($BeCO_3$)	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$	($RaCO_3$)
$-\Delta H^\circ_{298}$	(243)	260,4	283,5	290,5	288	(300)

(B) $MeO_{(solid)} + CO_2$ (gas) = $MeCO_3$ (solid)

q	(5,6)	23,5	42,5	55,7	61,0	(72)

4. Results of Investigation of Thermal Dissociation

In this paper we have already put forward a number of considerations supplementing our previously published results on the investigation of the thermal dissociation of beryllium carbonate [3]. In the latter we assumed, on the basis of earlier data, $\Delta H^\circ_{BeO} = 135$ kcal. Recently Cosgrove and Snyder [12] determined the heat of formation of BeO by a direct method to an accuracy of ± 0,1 kcal. With the aid of this value (143,3 kcal) and the heat of formation of CO_2 (94,030 kcal), we obtain according to our experimental data [3]:

$$Be_{(solid)} + C_{(graph.)} + {}^3/_2 O_{2(gas)} = BeCO_{3(solid)}, \quad \Delta H^\circ_{BeCO_3} = -243 \text{ kcal/mole}. \qquad (8)$$

Our evaluation involves extrapolation since $BeCO_3$ can exist in the pure form only at above the standard temperature. These values are therefore put in brackets in Tables 3 and 4.

Closer consideration must be given to the dissociation equilibrium of strontium carbonate. After our paper [5] had been published, Lander [15] examined the same system and did not report any new data in connection with thermal dissociation. For the first time, however, Lander investigated the heat capacity of strontium carbonate:

$$C_p = 21{,}41 + 8{,}56 \cdot 10^{-3}\, T - 3{,}396 \cdot 10^5\, T^{-2}$$

The values of the Σ-functions [16,17], calculated with the help of the above equation, and our earlier data for P_{CO_2}, diverge somewhat (for example Σ = 13,0 [5] and Σ = 15,6 [15] for 850°), but in practice this difference has little effect upon the final value of ΔF_{298} and ΔH_{298}. The results of Lander substantially confirm our results.

Consequently, the values $\Delta H_0 = -53885$ cal and I = 32,06 cal/mole, deg, and the values of the Σ-functions obtained by our method [5] can be directly utilized for calculation of ΔF_{298}. We preferred, however, in the first place to try out one more method of calculation of ΔH_0 and I, using the standard entropies of the reactants [13]. In this case we obtain $\Delta H_0 = -58125$ cal, I = 35,60 cal/mole. deg. Without showing preference either for the first or the second method, and taking a mean value, we find $\Delta H_0 = -56{,}000$ cal; I = 33,83 cal/mole. deg, which on substitution in the usual equations for dependence of ΔF and ΔH on temperature gives for standard conditions $\Delta F_{298} = -43{,}520$ and $\Delta H_{298} = -55710$.

The values obtained, which we calculated from investigations of the equilibrium at high temperatures, are in satisfactory agreement with those previously found by the calorimetric method ($\Delta F_{298} = -43{,}900$ cal and $\Delta H_{298} = -56{,}100$ cal [4]). Consequently, we may assume as a basis for the dissociation of strontium carbonate

$$SrCO_3\ (solid) = SrO\ (solid) + CO_2(gas) - 56{,}1 \pm 0{,}4\ (\pm 1\%) \qquad (9)$$

Introducing the heats of formation of SrO and CO_2 [13], we get

$$Sr_{(solid)} + C_{(graph.)} + {}^3/_2\,O_2(gas) = SrCO_3\ (solid) - 290{,}5\ \text{kcal/mole}. \qquad (10)$$

The foregoing considerations permit a generalization of the thermochemical data for the carbonates (Table 3) both for standard heats of formation (A) and for heats of dissociation (B). Data are also included for calcite from a critical survey of the thermal constants in 1949 [13]. The bracketed values are extrapolated results for radium (see theoretical part below) and for beryllium (see preceding section).

THEORETICAL

The experimental data for the thermochemistry of carbonates of metals of the second group in conjunction with literature data enable the establishment of a series of thermodynamic and crystallochemical constants not only for the carbonates themselves but also for the cations entering into their composition as well as for the carbonate ion.

1. Standard Free Energies of Thermal Dissociation of Carbonates

For the reaction $MeCO_3 \rightleftharpoons MeO + CO_2$ the values of ΔH_{298} that we found were given in Table 3 (B). Since

$$\Delta F_{298} = \Delta H_{298} - T\Delta S, \qquad (11)$$

the calculation of ΔF_{298} requires the value of the entropies of MeO, $MeCO_3$ and CO_2. These values appear in Kelley's survey [18], while the unmeasured value of S for $BeCO_3$ could be evaluated by Kireev's method [19]. In view of the instability of the pure carbonate and the uncertainty in the accuracy of the evaluations, the corresponding values of the constants for $BeCO_3$ are enclosed in brackets. In the following Table 4 is given our extrapolated value of ΔF_{298} for $RaCO_3$, whose accuracy is $\pm$ 4%.

TABLE 4

Standard Free Energies of Dissociation of Carbonates of the Second Group in kcal

Carbonate	$(BeCO_3)$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$	$(RaCO_3)$
$-\Delta F_{298}$	(−6.7)	11.0	31.1	43.5	48.8	(49)

2. Properties of Ions in Solution

The solubility product (L_p) at 25° for $MgCO_3$ is one of the least known. For this substance we actually obtained reliable thermochemical data with whose help it is not difficult to calculate L_p. The free energy of solution of the carbonate in water (ΔF_{298}) is the sum of the free energies of the processes:

$$MeCO_{3(solid)} = Me_{(solid)} + C_{(graph.)} + {}^3/_2O_2(gas) \qquad (12)$$

$$Me_{(solid)} + aq = Me^{\cdot\cdot}\ (aq), \qquad (13)$$

$$C_{(graph)} + {}^3/_2O_2(gas) + aq = CO_3^{\cdot\cdot}\ aq. \qquad (14)$$

The free energies of processes (13) and (14) are well-known [20]; concerning the energy of solution of process (12), this is found from equation (11) with the help of our data for $MgCO_3$ and the entropy of the reactants [13].

We then obtain:

$$L_p = 1{,}76 \cdot 10^{-5}\ (\text{at } 25°) \qquad (15)$$

This constant is given by a rigorous method on the basis of reliable thermodynamic data. We may note that in Landolt-Börnstein [21] the value given is queried, while Seidel [22], gives it for the trihydrate of the carbonate under a CO_2 pressure of 1 atm.; Bolländer [23], like Landolt, gives it for 12°. Of these values ($1{,}2 \cdot 10^{-3}$; $1 \cdot 10^{-5}$; $2{,}6 \cdot 10^{-5}$) the first is known to be inaccurate, the second relates to the trihydrate, and the third is not at standard temperature. We may therefore recommend our estimated value as the only one relating to pure crystalline $MgCO_3$ in water at 25°.

The entropy of the aqueous carbonate ion was found by Latimer, Pitzer and Smith [24] by studying the ionization of carbonic acid (− 13.0 ± 1.0 entropy unit). Since the dissociation equilibrium of carbonic acid in aqueous solution is a complex one, the accuracy of this value is doubtful. Moreover, we have at our disposal three simpler methods of establishing the entropy of the carbonate ion which are also independent of one another. Carrying out the summation for these three processes (12), (13) and (14) of the free energies and heats of reaction taken from our experimental data and from the literature [20,25] we obtain from equation (11) the change of entropy during dissolution of $MgCO_3$ in water:

$$MgCO_{3(solid)} = Mg^{\cdot\cdot}\ (aq) + CO_3^{\cdot\cdot}(aq), \quad \Delta S_{298} = -58{,}25\ \text{kcal/degree}, \qquad (16)$$

The entropy of $MgCO_3$(solid) was determined experimentally and found to be 15.7 ± 0.2 entropy units [13].

Since Latimer and co-workers [24] proposed two different values for the entropy of the magnesium ion, we calculated the S_{298} of the ion from our experimental data and found a value of −33.52 entropy units. Then from equation [16] we found for the carbonate ion in water: $S_{298} = -9.0$ entropy units. The considerable discrepancy between this value and that proposed by Latimer prompted us to repeat similar calculations starting from our own data for another carbonate ($BaCO_3$), which also gave a value of −9.0 entropy units. Since it might be feared that the calculations based on one and the same investigation are not sufficiently objective, we calculated the S_{298} of the carbonate ion from the data of Kapustinsky and Dezideryeva [4] for $SrCO_3$ and obtained $S_{298} = -9.1$ entropy units. Consequently one and the same value is obtained to an accuracy of 0.1 entropy unit by investigation of three different substances, so that we can regard the result of Latimer, Pitzer and Smith as inaccurate and we can propose for the entropy of CO_3'' aq the value $S_{298} = -9.0 \pm 0.1$ entropy units.

3. Crystallochemical Characteristics

By carrying out the Born-Haber cycle with utilization of our experimental values for the heats of formation of carbonates, we can obtain the energies of the crystal lattice of the carbonates (Table 5), and then, utilizing this value and the Goldschmidt radii of the cations, we can find from the equation of the energy of ionic lattices [26] the "thermochemical radius" of the carbonate ion. The last column of Table 5 shows the good constancy of this value, regardless of which of the carbonates we start from. The slight drop at the start of the group is explained by the effect, already described by one of us and Yatsimirsky [27], of introduction of a small cation into the interior of a non-spherical anion.

Table 5

"Thermochemical Radius" of the Carbonate Ion

Compound	Radius of cation, in A	Lattice energy from the Born-Haber cycle	Radius of CO_3''
$BeCO_3$	0.34	905	1.79
$MgCO_3$	0.78	770	1.82
$CaCO_3$	1.06	689	1.86
$SrCO_3$	1.27	657	1.84
$BaCO_3$	1.43	629	1.85

The mean value of the "thermochemical radius" of CO_3'' is r = 1.83 ± 0.02 A. This value agrees to within 0.5% with that calculated by Yatsimirsky [25].

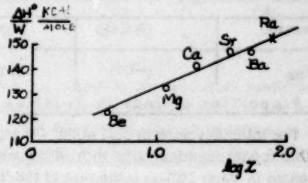

Fig. 5.

The energy of the crystal lattice (u) can also be represented as the square of the difference of the "crystallochemical electronegativities" of the cation $\kappa_{C^{\cdot\cdot}}$ and the anion $\kappa_{A^{\cdot}}$ [28]:

$$u = \Sigma(\kappa_{C^{\cdot\cdot}} - \kappa_{A^{\cdot}})^2, \qquad (17)$$

where Σ is the sum of the bonds. For cations of the 2nd group, the values of κ are known [28]. Substituting in the above formula the experimental lattice energies (Table 5) we find that value of κ for CO_3'' ion which best corresponds to the already known $\kappa_{C^{\cdot\cdot}}$.

In order to check the found $\kappa_{CO_3''} = 0.2$, it may be substituted in equation (17) and with the help of Table 5 we may calculate $\kappa_{C^{\cdot\cdot}}$; the values of the latter are found to agree to within 2% with the values previously assumed for all five cations.

4. The Rule of Thermochemical Logarithmicity

According to this rule [1], the heat of formation of compounds per gram-equivalent within each group for ions (atoms) of electronic analogs must be linearly dependent on the logarithm of the atomic number of the cation (log Z_C). This generalization, which establishes a link between thermochemistry and Mendeleev's periodic law and which is based on the concept of the electronic structure of the atom, makes provision for the possibility of deviation from linear dependence for $Be^{\cdot\cdot}$, as a two-electron ion in contrast to the ions with an 8-electron configuration which follow it. Whether, however, this deviation was considerable or minute could not previously be estimated since this

depends upon the nature of the ion. Figure 5, in which are plotted the heats of formation per gram-equivalent ($\Delta H/W$) as a function of the logarithm of $Z_{C^{2+}}$, shows that this deviation is so insignificant that it nearly coincides with the attainable margin of error. The rule of thermochemical logarithmicity is well confirmed by the experimental material for the thermochemistry of elements of the 2nd group, and we are therefore justified in graphically extrapolating the straight-line plot in order to ascertain the heat of formation of radium carbonate; for the latter we get $H^{\circ}_{298} = -300$ kcal.

SUMMARY

1. An investigation of the heats of solution of magnesium and barium in acid and a study of the thermal dissociation of the carbonates of beryllium ($BeCO_3 \cdot BeO$) and strontium has given the standard heats of formation and also the heats and free energies of thermal dissociation of the carbonates of Be, Mg, Sr and Ba (Tables 3 and 4).

2. With the help of the foregoing data and of the thermodynamic constants critically selected from the literature, calculations were made of the solubility product of $MgCO_3$ $L_p = 1.76 \cdot 10^{-5}$ at 25° and of the entropy of the carbonate ion ($CO^{=}_3$) $S_{298} = -9.0 \pm 0.1$ entropy units.

3. On the basis of the thermochemical data obtained and with the help of the calculated energy of the crystal lattice, values are found for the "thermochemical radius" of the $CO^{=}_3$ ion $r = 1.83 \pm 0.02$ A, and of the "crystallochemical electronegativity" of $CO^{=}_3$ $\kappa = 0.2$. Both of these magnitudes are in complete agreement with the experimental data for all the five above-mentioned carbonates.

4. Confirmation is obtained of the applicability of the rule of thermochemical logarithmicity to carbonates of elements of the second (main) group of the periodic system of Mendeleev. Extrapolation with the aid of this law gives for the heat of formation of radium carbonate a value of $\Delta H^{\circ}_{298} = -300$ kcal/mole.

Moscow Mendeleev Institute of Chemical Technology — Received November 11, 1953

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SYSTEMS CONTAINING CONCENTRATED HYDROGEN PEROXIDE

V. THERMAL CHARACTERISTICS OF THE SOLID PHASES OF THE SYSTEM Ca $(OH)_2$ - H_2O_2 - H_2O

S. Z. Makarov and N. K. Grigoryeva

In a study of the system $Ca(OH)_2 - H_2O_2 - H_2O$ over the temperature range of 0 to −21°, it was established [1] that the products of interaction of calcium hydroxide with hydrogen peroxide are undoubtedly the three solid phases: $CaO_2 \cdot 8H_2O$, $CaO_2 \cdot 2H_2O$ and $CaO_2 \cdot 2H_2O_2$.

In order to supplement the method of analytical examination, which was inadequate for full physicochemical characterization of the solid phases of the system, use was made of the methods of thermal analysis and X-ray examination; photomicrographs were also taken and a study was made of the thermal stability and of the processes of dehydration of the hydrated forms of calcium peroxide. The prepared peroxy compounds of calcium, also the anhydrous calcium peroxide and calcium hydroxide, were subjected to thermal anaylsis with the differential recorder, using a recording pyrometer of the Kurnakov type.

The heating curve of anhydrous calcium peroxide CaO_2 (Fig.1) is characterized by the presence of one endothermic effect corresponding to the breakdown of CaO_2 to CaO with evolution of active oxygen. Since the reaction of formation of CaO_2 is accompanied by heat evolution, an endothermic course of the decomposition reaction is entirely probable. Calcium peroxide contains 21.0% active oxygen.

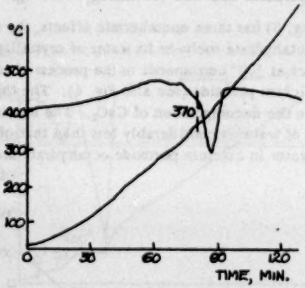

Fig. 1. Heating curve of CaO_2.

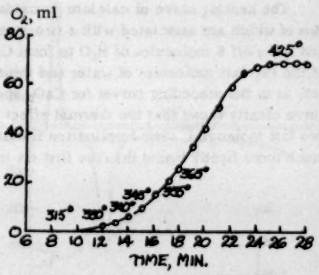

Fig. 2. Thermal stability of CaO_2 (check by amount of oxygen released)

For more accurate characterization of the thermal stability of CaO_2, observations were made, parallel with the recording of the heating curve, of the evolution of active oxygen. For this purpose, the vessel in which the heating was carried out was connected to a measuring buret containing water saturated with oxygen, and at definite intervals of time measurements were made of the volume of evolved gas as well as of the corresponding temperatures. Data for the measurements are set forth in Table 1 and plotted in Fig. 2.

The process of thermal decomposition was also checked from the determination of the content of active oxygen in the residue after heating of CaO_2 to a definite temperature at a heating velocity of 4-5° per min. (Table 2 and Fig. 3).

Table 1

Duration, in min.	Temp. °C	Amount of oxygen evolved, in ml	Duration, in min.	Temp. °C	Amount of oxygen evolved, in ml
68	315	0,8	81	-	51,0
71	330	2,4	82	-	59,4
73	340	4,2	83	-	65,6
74	345	7,2	84	-	68,0
76	355	16,0	85	425	69,0
78	365	26,0	86	-	69,0
79	-	35,0	89	-	69,0
80	-	43,0	90	-	69,0

Table 2

Heating temp., in °C	Amount of active oxygen evolved, in %	Heating temp., in °C	Amount of active oxygen evolved, in %
175	0,15	340	1,58
200	0,33	360	5,20
250	0,60	380	13,75
300	0,90	400	18,0
320	1,15	425	19,6

We see that up to 175° anhydrous calcium peroxide CaO_2 is completely stable; from 175 to 300° there is insignificant loss of active oxygen (approx. 0,9%), and only above 300° does intensive breakdown of CaO_2 take place as reflected by the corresponding thermal effect on the heating curve. Complete decomposition of CaO_2 is completed at 400-425°.

The heating curve of calcium peroxide dihydrate $CaO_2 \cdot 2H_2O$ (Fig. 4) has two endothermic effects: the first at 100° corresponds to dehydration of $CaO_2 \cdot 2H_2O$ with transformation into CaO_2 containing 18-19% active oxygen, while the second starts at above 300° and is complete at 400-425°, corresponding to the decomposition of anhydrous calcium peroxide into CaO (in analogy with Fig. 1).

The heating curve of calcium peroxide octahydrate $CaO_2 \cdot 8H_2O$ (Fig. 5) has three endothermic effects, the first two of which are associated with a two-stage dehydration. At 40° the octahydrate melts in its water of crystallization and splits off 6 molecules of H_2O to form $CaO_2 \cdot 2H_2O$. The second effect at 100° corresponds to the process of removal of the two last molecules of water and transformation into anhydrous calcium peroxide (see also Fig. 4). The third effect, as in the preceding curves for CaO_2 and $CaO_2 \cdot 2H_2O$, corresponds to the decomposition of CaO_2. The heating curve clearly shows that the thermal effect of removal of six molecules of water is considerably less than that of the two last molecules. The implication is that the two last molecules of water in calcium peroxide octahydrate are very much more firmly bound than the first six molecules.

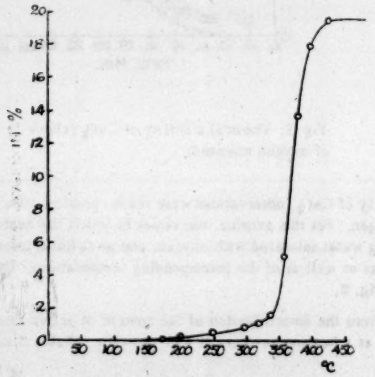

Fig. 3. Thermal stability of CaO_2 (check by oxygen content of residue).

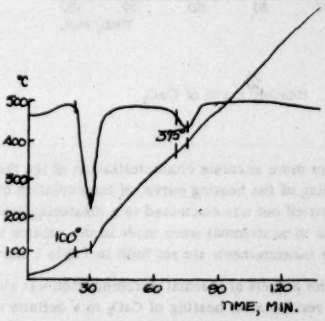

Fig. 4. Heating curve of $CaO_2 \cdot 2H_2O$.

The heating curves of $CaO_2 \cdot 8H_2O$ and $CaO_2 \cdot 2H_2O$ show that the two-stage successive dehydration of $CaO_2 \cdot 8H_2O$ proceeds with a like thermal effect, whereas de Forcrand [2], in examining the two stages of successive hydration of CaO_2 to $CaO_2 \cdot 2H_2O$ and to $CaO_2 \cdot 8H_2O$, observed unlike thermal effects, namely, he established that the binding of the first two molecules of H_2O to solid CaO_2 proceeds with absorption of –2,215 cal, while the addition of the six molecules of water proceeds with evolution of + 17,851 cal. On this basis he concluded that $CaO_2 \cdot 2H_2O$ is not a true hydrate of calcium peroxide but a combination of H_2O_2 with hydrated lime $Ca(OH)_2 \cdot H_2O_2$, which thus also accounts for the difference in properties. This theory was supported by Foregger and Philipp [3].

However, our plot of the heating curve of $CaO_2 \cdot 2H_2O$ conclusively points to a hydrated compound of calcium peroxide with an endothermic effect of dehydration. The presence of a molecule of H_2O_2 would have given an exothermic effect on the heating curve due to the evolution of active oxygen as is usually observed with perhydrates of peroxides.

The heating curve of the diperhydrate of calcium peroxide $CaO_2 \cdot 2H_2O_2$ (Fig. 6) is characterized by one exothermic effect and two endothermic effects. The specimen of $CaO_2 \cdot 2H_2O_2$ contained 31% active oxygen. This very oxygen-rich peroxy compound of calcium theoretically contains 34.4% active oxygen.

The exothermic effect at 40–45° is the result of evolution of active oxygen from the combined hydrogen peroxide, with transformation of the $CaO_2 \cdot 2H_2O_2$ into $CaO_2 \cdot 2H_2O$ according to the reaction: $CaO_2 \cdot 2H_2O_2 \rightarrow CaO_2 \cdot 2H_2O + O_2$.

At this point it is pertinent to mention that the direction of this reaction is associated with the evolution of active oxygen and not with the transformation of $CaO_2 \cdot 2H_2O_2$ into $CaO_2 \cdot 2H_2O$. Later an endothermic effect is observed which corresponds to dehydration and transformation into CaO_2, and, finally, the last effect is bound up with the breakdown of CaO_2 to CaO.

Simultaneously with the recording of the heating curve of $CaO_2 \cdot 2H_2O_2$, a study was made of the process of its thermal decomposition which was checked by the evolution of active oxygen. The results are set forth in Table 3 and the decomposition curve is shown in Fig. 7.

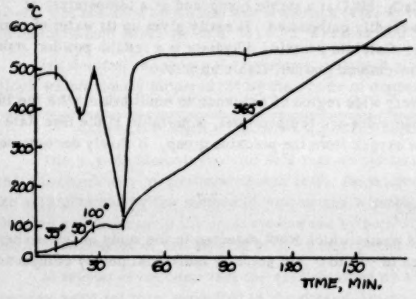

Fig. 5. Heating curve of $CaO_2 \cdot 8H_2O$

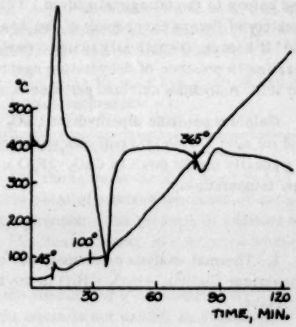

Fig. 6. Heating curve of $CaO_2 \cdot 2H_2O_2$

Table 3

Period, in min.	Temp., in °C	Amount of oxygen, in ml	Period, in min.	Temp., in °C	Amount of oxygen, in ml	Period, in min.	Temp., in °C	Amount of oxygen, in ml
16	48	0,2	23	70	102,0	96	–	111,0
17	51	1,0	30	95	102,0	98	–	115,0
18	54	3,0	87	335	102,2	100	–	118,0
19	57	5,0	88	340	103,0	102	–	122,0
20	60	12,0	90	350	104,0	104	400	124,0
21	63	30,0	92	–	106,0	106	–	124,2
22	65	97,0	94	–	108,0	108	–	124,2

The data show that the process of thermal decomposition of $CaO_2 \cdot 2H_2O_2$ to $CaO_2 \cdot 2H_2O$ proceeds exceptionally rapidly with great evolution of heat; at above 300° complete decomposition of calcium peroxide takes place. For the purpose of comparison the heating curve of calcium hydroxide $Ca(OH)_2$ was plotted (Fig. 8); this has one endothermic effect at 530-540°, corresponding to a dissociation different from that previously described.

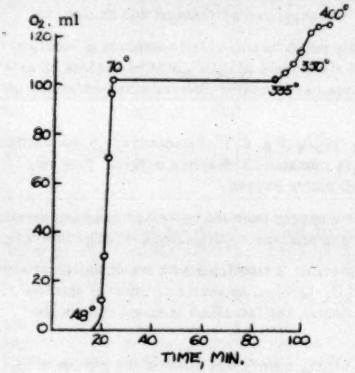

Fig. 7. Thermal decomposition of $CaO_2 \cdot 2H_2O_2$ (check by evolution of oxygen).

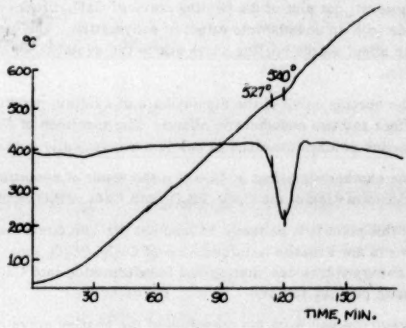

Fig. 8 Heating curve of $Ca(OH)_2$.

According to recent data of Shinemann and King [4] on the structure of $CaO_2 \cdot 8H_2O$, the crystals of this compound belong to the tetragonal system. This is confirmed by photomicrographs and X-ray data obtained in the Laboratory of Peroxy Compounds of the Acad. Sci. USSR. $CaO_2 \cdot 8H_2O$ is a stable compound at a temperature of 35-40° if kept in hermetically sealed vessels; in the air it is readily carbonated. It easily gives up its water of crystallization in presence of dehydrating agents and on heating. Calcium peroxide dihydrate is a reddish powder, stable up to 100°. Anhydrous calcium peroxide is a very fine, cream-colored powder, stable up to 300°

Calcium peroxide diperhydrate $CaO_2 \cdot 2H_2O_2$, with a very wide region of existence in equilibrium with the liquid phase over a wide range of concentrations of hydrogen peroxides and temperatures, is unstable in the free state and gradually breaks down to $CaO_2 \cdot 2H_2O$ with loss of active oxygen from the peroxide group. It slowly decomposes at low temperatures.

SUMMARY

1. Thermal analysis confirmed that all the three solid phases which were detected in the study of the isotherms of the system $Ca(OH)_2 - H_2O_2 - H_2O$ in the temperature range of –21 to 0° are actually individual peroxy compounds of calcium.

2. The octahydrate $CaO_2 \cdot 8H_2O$ and the dihydrate $CaO_2 \cdot 2H_2O$ of calcium peroxide are readily dehydrated and are converted into anhydrous calcium peroxide which is stable up to 300°

3. The diperhydrate of calcium peroxide $CaO_2 \cdot 2H_2O_2$, which exists over a wide region in equilibrium with the liquid phase, is unstable in the free state and readily breaks down with formation of $CaO_2 \cdot 2H_2O$.

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Received August 8, 1953

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THE ALLYL REARRANGEMENT IN THE POLYCHLOROBUTENOIC ACID SERIES

AND SOME ERRORS BY AUWERS AND WISSEBACH IN THEIR PAPERS [1,2]

A. N. Nesmeyanov, L. I. Zakharkin, V. N. Kost and R. Kh. Freidlina

In the previous communication [3] we showed that although trichloropropenes with the structure $CCl_2CH = CH_2$ and $CCl_2 = CH-CH_2Cl$ do not exist in a state of reciprocal isomerization equilibrium, in a large number of exchange reactions they nevertheless form one and the same products with the structure $CCl_2=CH-CH_2X$, where X is a nucleophilic group exchanging with halogen, regardless of which of the two trichloropropenes is brought into reaction. This is true of the reactions of both trichloropropenes with diethylamine, sodium ethyoxide, sodium sulfide, sodium acetate, sodium malonic ester, copper cyanide, organomagnesium compounds, etc. In the course of these reactions 1,1,1-trichloropropene undergoes an anionotropic allyl rearrangement. We regard the exchange reactions of 1,1,1-trichloropropene as involving the mechanism of "transfer of the reaction center" [4] at the system of δ,π-conjugated bonds in accordance with schemes (1) and (2):

$$Cl-CCl_2-CH=CH_2 + \oplus X \longrightarrow Cl^- + CCl_2=CH-CH_2X \qquad (1)$$

$$CCl_3-CH=CH_2 + \dot{X}_1 \longrightarrow CCl_3-\dot{C}H-CH_2X_1 \longrightarrow CCl_2=CH-CH_2X_1 + \dot{C}l \qquad (2)$$

(compare with [5]).

In the present research we have studied the reciprocal relations of acids with the structure $CHCl_2-CH=CH-CO_2H$ and $CCl_2=CH-CH_2CO_2H$ and the corresponding behavior of their derivatives — involving a prototropic allylic rearrangement. In the literature are described two γ,γ-dichlorocrotonic acids. A γ,γ-dichlorocrotonic acid with m.p. 42-43° was obtained by Auwers and Wissebach [1,2] by reducing γ,γ,γ-trichlorocrotonic acid (see also [6]). A γ,γ,-dichlorocrotonic acid with m.p. 101-102° was obtained from dichloroacetaldehyde and malonic acid [7].

We decided to prepare the previously unknown γ,γ-dichlorovinylacetic acid* by mild hydrolysis of its nitrile which we previously prepared [3] by the action of copper cyanide on 1,1,3-trichloropropene - 1:

$$CCl_2=CH-CH_2Cl + CuCN - CCl_2=CH-CH_2CN \xrightarrow[H^+]{H_2O} CCl_2=CH-CH_2-COOH$$

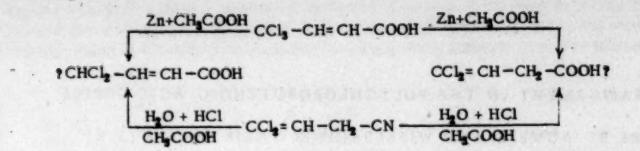
The γ,γ-dichlorovinylacetic acid that we systhesized melts at 42-43°, the same as the acid described by Auwers and Wissebach as γ,γ-dichlorocrotonic acid. Determination of the melting point of a mixed specimen of our acid and the acid obtained by the method of Auwers and Wissebach did not give a depression. The products of addition of chlorine and bromine to the acids systhesized by both methods also were identical products, as confirmed by the absence of depression of the melting point in mixed tests.

In support of the view that the acid obtained by both methods has the structure of γ,γ-dichlorovinylacetic acid, we may point out that, according to the data of Auwers and Wissebach, its esters do not exhibit an exaltation of molecular refraction, while its hydrolysis in presence of conc. H_2SO_4 leads to succinic acid. Opposing this view, on the other hand, is the reduction by the cited authors of the acid under the action of sodium amalgam to form crotonic acid. The problem is further complicated by the fact that Auwers and Wissebach [2], starting from the acid synthesized by them, obtained a nitrile via the chloride and amide; in its constants this nitrile differed from the nitrile of γ,γ-dichlorovinylacetic acid and exhibits an exaltation of molecular refraction. Repetition of the synthesis of these derivatives by the procedure of the cited authors, starting from specimens of acids prepared by both routes, led to one and the same acid chloride, amide, and nitrile regardless of the origin of the starting acid. However, only the constants of the acid chloride fully agreed with those described, whereas the constants of the amide and nitrile differed.

Since the structure of the starting substances for the synthesis of the unsaturated dichloro acid by both methods has been conclusively established (the structure of γ,γ,γ-trichlorocrotonic acid was established by its acid hydrolysis to fumaric acid; that of the nitrile of γ,γ-dichlorovinylacetic acid by acid hydrolysis to succinic acid), we must assume that one and the same acid could only be obtained as the result of rearrangement either in the process of reduction of the trichlorocrotonic acid or in the process of hydrolysis of the nitrile in question, as we see from the

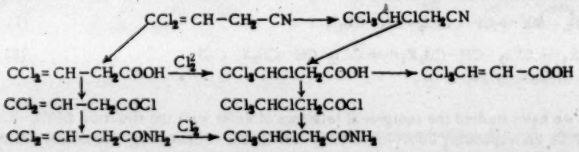
* Vinylacetic acid = 3-butenoic acid. Publisher.

following scheme:

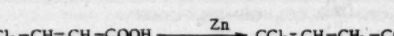


We arrived at a solution of this problem on the basis of the following considerations. On the one hand, the addition of chlorine to the nitrile of γ,γ-dichlorovinylacetic acid gave the nitrile of β,γ,γ,γ-tetrachlorobutyric acid from which the corresponding acid, the chloride and the amide, were then obtained by the usual method. Isomerization is very improbable in the first stage of this chain of transformations, while in the remaining stages it is obviously excluded. The structure of β,γ,γ,γ,-tetrachlorobutyric acid was proved by its dehydrochlorination to γ,γ,γ-trichlorocrotonic cid, identical with that described by Auwers and Wissebach and unambiguous in structure, so that the possibility of isomerization during the first stage is also excluded.

On the other hand, the investigated dichloro acid obtained by acid hydrolysis of the nitrile of γ,γ-dichlorovinylacetic acid was transformed by the usual routes into chloride, amide and nitrile (the latter proved to be identical with the starting nitrile). Addition of chlorine to this acid, its amide and nitrile led to formation of compounds identical with the above-described β, γ,γ,γ-tetrachlorobutyric acid and its derivatives. These results are summarized in the scheme:



These data show that the above-mentioned acid has the structure of γ,γ,-dichlorovinylacetic acid and that isomerization does not take place in the course of its preparation from the nitrile and in the course of its transformations in the conditions described in the experimental part. Consequently, on reduction of γ,γ,γ,-trichlorocrotonic acid under the action of zinc and glacial acetic acid in ethyl alcohol, there is formed not γ,γ,-dichlorocrotonic acid, as Auwers and Wissebach believed, but γ,γ-dichlorovinylacetic acid, i.e. the reduction takes place with rearrangement:



Dichlorovinylacetic acid is incapable of further reduction in the same conditions [1].

We also succeeded in explaining the fact, at first inexplicable, that γ,γ-dichlorovinylacetic acid is reduced to crotonic acid with the help of sodium amalgam [1]. We found that γ,γ-dichlorovinylacetic acid, its amide and nitrile are easily isomerized under the action of a base (e.g triethylamine) to γ,γ-dichlorocrotonic acid and its derivatives. The obtained γ,γ-dichlorocrotonic acid proved to be identical with the acid synthesized from dichloroacetaldehyde and malonic acid [7], which fact confirmed its structure. Since the reduction of γ,γ-dichlorovinylacetic acid by Auwers and Wissebach was effected under the action of sodium amalgam, conditions were created for its isomerization to γ,γ-dichlorocrotonic acid and for its further reduction to crotonic acid.

The tranformation of γ,γ,γ-trichlorocrotonic acid, on the one hand, by hydrolysis to fumaric acid, and, on the other hand, by reduction to crotonic acid is cited in modern monographs on stereochemistry and in textbooks of organic chemistry as a strict proof of the trans-structure of crotonic acid and as an example of the establishment of the geometrical configuration by transformation into a derivative of known configuration by reactions which leave intact the olefinic carbon linkages. Now we see that the two-stage reduction of γ,γ,γ-trichlorocrotonic acid to crotonic acid, which was carried out by Auwers and Wissebach, proceeds with a twofold isomerization which was not observed by the authors, and therefore it cannot serve to establish the configuration of crotonic acid. We also see that the allylic rearrangement introduces substantial limitations into the method of establishment of the configuration based on transformation into a derivative with a known spatial structure.

Our preparations of acid chloride amides and nitriles of both γ,γ-dichlorovinylacetic acid and of γ,γ-dichlorocrotonic acid permitted us to establish that the acid chloride described by Auwers and Wissebach is the chloride of γ,γ-dichlorovinylacetic acid, while the amide and nitrile described by them are derivatives of γ,γ-dichlorocrotonic acid. It is evident that in the process of transformation of γ,γ-dichlorovinylacetyl chloride into an amide an

isomerization not detected by the authors took place with formation of the amide of γ,γ-dichlorocrotonic acid.

It should be noted that neither of the series of the derivatives studied of the type of $CCl_2{=}CH{-}CH_2X$ and $CHCl_2CH{=}CH{-}X$ isomerizes in an acid medium. Thus, on hydrolysis of the nitrile of γ,γ-dichlorovinylacetic acid in a mixture of hydrochloric and acetic acids, γ,γ-dichlorovinylacetic acid was obtained, while hydrolysis of γ,γ-dichlorocrotonitrile in the same conditions gave γ,γ-dichlorocrotonic acid. The same must be said about γ,γ,γ-trichlorocrotonic acid, which hydrolyzes without isomerization in a strongly acidic medium with formation of fumaric acid. Hence it follows that the preparation by Auwers and Wissebach of γ,γ-dichlorovinylacetic acid on reduction of γ,γ,γ-trichlorocrotonic acid in an acid medium cannot be explained either by preliminary isomerization of the starting acid or by the hypothesis of intermediate formation of γ,γ-dichlorocrotonic acid followed by the latter's isomerization. It is evident that the rearrangement takes place in the very process of reduction. We suggest that this reaction also proceeds according to the mechanism of "transfer of the reaction center" as follows:

$$CCl_3{-}CH{=}CH{-}COOH + H \rightarrow CCl_2\dot{C}HCH_2COOH \rightarrow CCl_2{=}CH{-}CH_2{-}COOH + \dot{C}l.$$

EXPERIMENTAL

Saponification of γ,γ-dichlorovinylacetonitrile. γ,γ-Dichlorovinylacetonitrile was prepared by the action of copper cyanide on 1,1,3-trichloropropene-1 [3]. A solution of 35 g γ,γ-dichlorovinylacetonitrile in 65 ml glacial acetic acid, 30 ml conc. HCl and 30 ml water was boiled for 5 hours. After cooling, water was added and the product extracted with chloroform. The solvent was driven off and the residue distilled in vacuum. B.p. of γ,γ-dichlorovinylacetic acid 111-112° (7mm); m.p. 42-43° (from ligroine); yield 38 g (95% of theory).

	Found %	C 31.22; 31.26;	H 2.70; 2.63
$C_4H_4O_2Cl_2$.	Calculated %	C 31.01	H 2.57

The acid does not give a melting point depression in a mixed test with the acid obtained by reduction of γ,γ,γ-trichlorocrotonic acid [1,2].

β,γ-Dibromo-γ,γ-dichlorobutyric acid is obtained in quantitative yield by addition of bromine to γ,γ-dichlorovinylacetic acid under irradiation; m.p. 121-122°. The acid does not give a melting point depression with the dibromodichlorobutyric acid prepared by addition of bromine to the acid formed by reduction of γ,γ,γ-trichlorocrotonic acid [1,2].

β,γ,γ,γ-Tetrachlorobutyric acid is obtained in quantitative yield by addition of chlorine to γ,γ-dichlorovinylacetic acid in chloroform solution under irradiation; m.p. 108-109°.

	Found %	C 21.42; 21.66;	H 1.56; 1.61
$C_4H_4O_2Cl_4$.	Calculated %	C 21.24;	H 1.76

The acid does not give a melting point depression in a mixed test with the acid obtained by saponification of γ,γ,γ-tetrachlorobutyronitrile.

Saponification of β,γ,γ,γ-tetrachlorobutyronitrile. β,γ,γ,γ-Tetrachlorobutyronitrile was obtained by addition of chlorine to γ,γ-dichlorovinylacetonitrile in chloroform solution under irradiation [3]. A solution of 8 g β,γ,γ,γ-tetrachlorobutyronitrile in 20 ml acetic acid, 10 ml conc. HCl and 10 ml water was boiled for 8 hours. After cooling, water was added and the product extracted with chloroform. The solvent was driven off and the solid residue recrystallized from a mixture of benzene and ligroine; m.p. 108-109°; yield 7.9 g (91% of theory).

Dehydrochlorination of β,γ,γ,γ-tetrachlorobutyric acid. 6.8 g β,γ,γ,γ-tetrachlorobutyric acid was dissolved in an aqueous solution of NaOH (3 g NaOH in 25 ml water) and the solution stood at room temperature for 5 hours. The solution was then acidified with hydrochloric acid and extracted with ether. The ethereal extract was dried with calcium chloride. After driving off the ether, the solid residue was recrystallized from ligroine, m.p. 113-114°; yield 3.8 g (67% of theory). The acid obtained does not give a depression of m.p. in a mixed test with an authentic specimen of γ,γ,γ-trichlorocrotonic acid.

β,γ,γ,γ-Tetrachlorobutyrylchloride is prepared in quantitative yield by 4 hours' boiling of β,γ,γ,γ-tetrachlorobutyric acid with twice the weight of thionyl chloride. The chloride has b.p. 69-70° (2.5 mm); n_D^{20} 1.5130; d_4^{20} 1.6129; found MR 45.53; Calculated for $C_4H_2Cl_5O$ MR 45.39.

β,γ,γ,γ-Tetrachlorobutyramide was obtained by saturating an ethereal solution of the chloride with ammonia at 0°. After the ether had been driven off, the crystalline residue was extracted with hot benzene. On cooling the benzene deposits the amide which after recrystallization has m.p. 138-138.5°.

Found %: N 6.18; 6.23

$C_4H_3NCl_4O$. Calculated %: N 6.22

γ,γ-Dichlorovinylacetyl chloride. A solution of 20 g γ,γ-dichlorovinylacetic acid in 80 g thionyl chloride was heated 4 hours on a water bath. The excess of thionyl chloride was driven off and the residue distilled in vacuum. Yield 21 g (95% of theory) of γ,γ-dichlorovinylacetyl chloride with b.p. 67-68° (13 mm); n_D^{20} 1.4995.

γ,γ-Dichlorovinylacetamide. Into a cooled solution of 20 g γ,γ-dichlorovinylacetyl chloride in 75 ml absolute ether was passed dry ammonia until saturated. After the ether had been driven off, the crystalline residue was extracted several times with hot benzene. On cooling, the benzene solution deposited the amide in the form of plates; m.p. 93-94° (from benzene); yield 16 g (90 % of theory).

Found %: N 9.02; 9.15

$C_4H_5ONCl_2$. Calculated %: N 9.09

The amide does not give a depression of melting point in admixture with the amide prepared by the same route from the acid of Auwers and Wissebach.

Addition of chlorine led to a quantitative yield of β,γ,γ,γ-tetrachlorobutyramide with m.p. 138°; it did not give a depression of melting point with a specimen of the β,γ,γ,γ-tetrachlorobutyramide prepared as described above from β,γ,γ,γ-tetrachlorobutyric acid.

Dehydration of γ,γ-dichlorovinylacetamide. A mixture of 10 g γ,γ-dichlorovinylacetamide and 14.5 g phosphorus pentoxide was heated in vacuum at 60° for an hour. The resultant nitrile was distilled off and had b.p. 87° (17 mm): n_D^{20} 1.4842; d_4^{20} 1.3148; found MR 29.60; calculated for $C_4H_3Cl_2N$ MR 29.76. These constants are in good agreement with those for γ,γ-dichlorovinylacetonitrile prepared by the action of copper cyanide on 1,1,3-trichloropropene-1 [3]; n_D^{20} 1.4842; d_4^{20} 1.3142; yield 7.5 g (85 % of theory).

The identity between these two nitriles was established by adding chlorine to them, when one and the same β,γ,γ,γ-tetrachlorobutyronitrile was obtained with m.p. 44°. A mixed sample did not give a m.p. depression.

Isomerization of γ,γ-dichlorovinylacetonitrile under the action of triethylamine. To 5 g of γ,γ-dichlorovinylacetonitrile was added 5 drops triethylamine. The mixture was stood at room temperature overnight. Distillation of the product gave 3 g γ,γ-dichlorocrotonitrile with b.p. 90-91° (18 mm); n_D^{20} 1.4970; d_4^{20} 1.3055; found MR 30.49; calculated for $C_4H_3Cl_2N$ MR 29.76. Auwers and Wissebach give [2]: n_D^{20} 1.4973; d_4^{20} 1.3049.

Hydrolysis of γ,γ-dichlorocrotonitrile. A solution of 2 g γ,γ-dichlorocrotonitrile in 5 ml acetic acid, 2 ml conc. HCl and 3 ml water was refluxed for 6 hours. After cooling, water was added and the product extracted with chloroform. The solvent was removed and the residue distilled in vacuum. The 140-145° (20 mm) fraction was collected. Yield 1.6 g crystalline product which after recrystallization from a mixture of benzene and ligroine had m.p. 99-100°. Yield 70% of theory.

Isomerization of γ,γ-dichlorovinylacetic acid. 3 g acid was heated with 2.1 g triethylamine on a water bath at 75-80° for 4 hours. At the commencement of heating the mass was liquid, but subsequently crystals gradually came down. After cooling, dilute hydrochloric acid was added to the reaction mass; the oil which settled out was extracted with chloroform. The solvent was driven off and the solid residue distilled in vacuum; b.p. 101-102° (4 mm). The acid crystallized in the condenser; yield 2.1 g (70% of theory); m.p. 99-100° (from benzene-ligroine).

The acid does not give a depression of melting point in admixture with the acid obtained by hydrolysis of γ,γ-dichlorocrotonitrile.

Isomerization of γ,γ-dichlorovinylacetamide. A solution of 0.6 g amide (m.p. 93-94°) in 10 ml benzene and 3 drops triethylamine was refluxed 4 hours. To the hot solution was added ligroine; on cooling the γ,γ-dichlorocrotonamide came down as needles; m.p. 81-82° (the amide described by Auwers and Wissebach melted at 82-83°) yield 0.5 g (83% of theory). The melting point of a mixture with the original amide was 58-60°.

SUMMARY

1. γ,γ-Dichlorovinylacetic acid was prepared by hydrolysis of its nitrile. The chloride and amide of the acid were prepared by the usual methods.

2. It was shown that, under the action of bases, γ,γ-dichlorovinylacetic acid and its amide and nitrile isomerize to γ,γ-dichlorocrotonic acid and its amide and nitrile.

3. Both series of derivatives of the type of $CCl_2=CH-CH_2X$ and $HCCl_2CH=CH-X$ (X = −COOH, −CN) do not isomerize under the action of acids.

4. It was established that the acid obtained by Auwers and Wissebach by reduction of γ,γ,γ-trichlorocrotonic acid with zinc and acetic acid in ethyl alcohol is not γ,γ-dichlorocrotonic acid, as assumed by the authors, but γ,γ-dichlorovinylacetic acid.

5. It was shown that the two-step reduction by Auwers and Wissebach of γ,γ,γ-trichlorocrotonic acid to crotonic acid proceeds with a double isomerization which was not detected by these authors. Consequently the reduction of γ,γ,γ-trichlorocrotonic acid to crotonic acid, which was performed by Auwers and Wissebach, cannot serve to establish the configuration of crotonic acid.

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Received August 23, 1953

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DERIVATIVES OF UNSATURATED PHOSPHINIC ACIDS

I. SYNTHESIS OF CHLORIDES OF β-ALKOXY (PHENOXY) - VINYL - PHOSPHINIC ACIDS

K. N. Anisimov and A. N. Nesmeyanov

The addition of salts of mercury to vinylethers (and esters), studied by one of us and Lutsenko [1], proceeds in such a manner that the mercury is attached to the olefinic carbon linkage, while the alkyl radical of the vinyl ether links with oxygen and acquires a carbonyl function

$$ROCH{=}CH_2 + HgAC_2 \rightarrow AcHg{-}CH_2{-}CHO.$$

In the present paper we investigate the addition of phosphorus pentachloride to alkyl (aryl) vinyl ethers and study the properties of the resultant addition products. The reaction of addition of phosphorus pentachloride to unsaturated compounds was discovered by March and Gardner [2] who showed that camphene reacts with phosphorus pentachloride to give an addition product forming, after treatment with water, camphenephosphinic acid.

Harnist [3] added phosphorus pentachloride to styrene, diphenylethylene, isobutene and ethynylbenzene. Bulle [4] carried out the reaction of phosphorus pentachloride with indene. Bergman and Bondi [5] made a fairly detailed study of the addition of phosphorus pentachloride to a series of unsaturated aromatic compounds; they established that addition of phosphorus pentachloride readily takes place, mainly to unsymmetrically phenylated ethylenes.

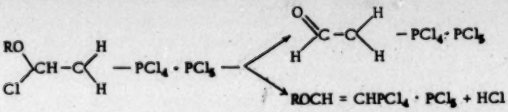
The same line of investigation was followed by Kosolapoff [6] and Bachmann [7] who showed that addition of phosphorus pentachloride to the double bond proceeds in such a way that the PCl_4 group adds on to the most hydrogenated carbon atom while an atom of chlorine adds on to the least hydrogenated carbon. The products of addition are isolated in the form of double compounds with phosphorus pentachloride.

The addition of phosphorus pentachloride to vinyl ethers has not hitherto been investigated. It was established that gradual addition of vinyl ethers to a suspension of phosphorus pentachloride in benzene leads to a very violent reaction with formation of a solid, crystalline product of addition from which gaseous hydrogen chloride begins to come off more intensively the higher the temperature of the reaction mass. Addition of phosphorus pentachloride to vinyl ethers follows the Markovnikov rule. In this manner we obtained products of addition of phosphorus pentachloride to methyl vinyl, ethyl vinyl, n-propyl vinyl, isopropyl vinyl, n-butyl vinyl, isobutyl vinyl, isoamyl vinyl, n-hexyl vinyl and phenyl vinyl ethers. The addition compounds are crystalline substances which lose hydrogen chloride at room temperature and are extremely easily hydrolyzed in the air. These properties prevented us from isolating the compounds in the pure state. Subsequently the addition products were worked up with sulfur dioxide (Michaelis [8]) until completely transformed into liquid. After the solvent, the phosphorus oxychloride and the thionyl chloride had been driven off, the residue was kept in the vacuum of a water jet pump on a boiling water bath until the whole of the hydrogen chloride was split off; it was fractionated in vacuum to give the chlorides of the β-alkoxy (phenoxy)-vinylphosphinic acids. The reactions are expressed by the following equations:

$$ROCH{=}CH_2 + 2PCl_5 = ROCHCl{-}CH_2PCl_4 \cdot PCl_5;$$

$$ROCHCl{-}CH_2PCl_4 \cdot PCl_5 + 2SO_2 = ROCH{=}CHPOCl_2 + POCl_3 + 2SOCl_2 + HCl\,.$$

Thus the addition of phosphorus pentachloride to vinyl ethers proceeds just like the addition to other compounds with an olefinic bond and quite differently to the addition of mercury salts. The dimeric molecule, P_2Cl_{10}, adds on; the alkyl radical of the alkoxyl remains intact and hydrogen chloride is split off with regeneration of the unsaturated structure of the vinyl ether. After the addition of phosphorus pentachloride the hydrogen atoms of the methylene linkage are found to be extremely mobile and of the two possible parallel reactions only one is realized, namely, the one involving cleavage of this hydrogen as HCl



We made use of this reaction for the synthesis of a large number of diverse functional derivatives of alkoxyvinylphosphinic acids.

EXPERIMENTAL

Vinyl ethers were prepared by the method of Favorsky and Shostakovsky [9]. Chlorides of β-alkoxyvinylphosphinic acids were synthesized in the following manner. Experiments were carried out in a dry flask protected against atmospheric moisture by a calcium chloride tube. To a weighed amount of 0.4 mole phosphorus pentachloride in 150 ml dry benzene was gradually added from a dropping funnel, with shaking and water cooling, 0.2 mole alkyl vinyl ether. Considerable heat was developed and a dense crystalline precipitate was formed; a short time after the whole of the ether had been run in, the precipitate started to give off hydrogen chloride. The following day sulfur dioxide was passed into the product at room temperature until the crystalline precipitate was completely transformed into a liquid. The reaction proceeded with heat development; cooling was sometimes employed. The product was transferred to a Claisen flask and the benzene, $POCl_3$ and $SOCl_2$ were distilled off in vacuum; the mixture was kept in the vacuum of a water jet pump on a hot water bath until the whole of the HCl had split off and the residue was then fractionated in vacuum. This method was used for the synthesis of the chlorides of the β-alkoxy (phenoxy)-vinyl phosphinic acids whose properties are set forth in the table.

β-Methoxyvinylphosphinyl chloride $CH_3OCH = CHPOCl_2$. Into the previously prepared addition product ($CH_3OCHCl-CH_2PCl_4PCl_5$) was passed SO_2 until transformation of the crystalline mass into a liquid. After the solvent, the $POCl_3$ and $SOCl_2$ had been driven off, the residue was fractionated in vacuum. β-Methoxyvinylphosphinyl chloride has b.p. 76° (1.5 mm); n_D^{20} 1.5052; d_4^{20} 1.4186.

	Found %	P 17.38; 17.33;	C 20.17; 20.49;	H 2.62; 2.62;	Cl 40.65; 40.18	
$C_3H_5O_2Cl_2P$.	Calculated %	P 17.71	C 20.57;	H 2.85;	Cl 40.57	

TABLE

Formula	B.p. in °C (p in mm. mercury column)		n_D^{20}	d_4^{20}	Yield in %
$CH_3-O-CH = CHPOCl_2$	76	(1.5)	1.5052	1.4186	11
$C_2H_5-O-CH = CHPOCl_2$	84	(2)	1.4989	1.3221	87
n-$C_3H_7-O-CH = CHPOCl_2$	101	(3)	1.4945	1.2823	78
i-$C_3H_7-O-CH = CHPOCl_2$	m.p. 52–53				76
n-$C_4H_9-O-CH = CHPOCl_2$	107.5	(2)	1.4926	1.2384	81
i-$C_4H_9-O-CH = CHPOCl_2$	96	(1)	1.4900	1.2318	78
$(CH_3)_2CH-(CH_2)_2O-CH=CHPOCl_2$	112	(1)	1.4876	1.2058	95
n-$C_5H_{11}O-CH = CHPOCl_2$	126	(2)	1.4890	1.2083	92
$C_6H_5-O-CH = CHPOCl_2$	131	(2)	1.5708	1.3710	75

β-Ethoxyvinylphosphinyl chloride $C_2H_5OCH = CHPOCl_2$. SO_2 was passed into the product of addition ($C_2H_5-OCHCl-CH_2PCl_4 \cdot PCl_5$) until the substance had turned liquid the solvent, $POCl_3$ and $SOCl_2$ were then distilled off at the ordinary pressure and the residue at 2 mm. Yield 33 g (87% of theory) with b.p. 84.5–85° (2 mm); n_D^{20} 1.4989; d_4^{20} 2.3321.

	Found %	P 16.19; 16.47;	C 37.18; 37.45			
$C_4H_7O_2Cl_2P$.	Calculated %	P 16.40;	C 37.56			

β-n-Propoxyvinylphosphinyl chloride n-$C_3H_7OCH = CHPOCl_2$. The chloride was synthesized in the above-described conditions. Yield 32 g (78% of theory) with b.p. 101° (3 mm); n_D^{20} 1.4925; d_4^{20} 1.2823.

	Found %	P 15.44; 15.26;	C 29.98; 30.21;	H 3.95; 3.90;	Cl 34.81; 34.92	
$C_5H_9O_2Cl_2P$.	Calculated %	P 15.27	C 29.55;	H 4.43	Cl 34.97	

β-Isopropoxyvinylphosphinyl chloride i-$C_3H_7OCH = CHPOCl_2$. Synthesis conditions as above. Yield 31 g chloride (76% of theory) with b.p. 92° (3 mm); m.p. 52-53°.

Found %: P 15.37; 15.00; C 29.73; 29.40; H 4.28; 4.46; Cl 34.94; 34.91
$C_5H_9O_2Cl_2P$. Calculated %: P 15.27; C 29.55; H 4.43; Cl 34.97

β-n-Butoxyvinylphosphinyl chloride n-$C_4H_9OCH = CHPOCl_2$. The synthesis was effected in the above-described conditions. Yield 35.5 g (81% of theory) with b.p. 107.5° (2 mm); n_D^{20} 1.4926; d_4^{20} 1.2384.

Found %: P 14.14; 14.27; Cl 32.60; 32.80
$C_6H_{11}O_2Cl_2P$. Calculated %: P 14.28 Cl 32.71

Isobutoxyvinylphosphinyl chloride i-$C_4H_9OCH = CHPOCl_2$. Preparation by the above-described method. Yield 34 g (78% of theory) with b.p. 96° (1 mm); n_D^{20} 1.4900; d_4^{20} 1.2318.

Found %: P 14.43; 14.24; C 33.26; 33.36; H 4.95; 5.10; Cl 32.56; 32.78
$C_6H_{11}O_2Cl_2P$. Calculated %: P 14.28; C 33.17; H 5.06; Cl 32.71

β-Isoamyloxyvinylphosphinyl chloride $(CH_3)_2CH-CH_2-CH_2OCH = CHPOCl_2$. Same conditions for preparation. 44 g was synthesized (95% of theory) with b.p. 112° (1 mm); n_D^{20} 1.4876; d_4^{20} 1.2058.

Found %: C 36.19; 36.42; H 5.62; 5.30; P 13.23; 13.20
$C_7H_{13}O_2Cl_2P$. Calculated %: C 36.36; H 5.62; P 13.41

β-n-Hexyloxyvinylphosphinyl chloride n-$C_6H_{13}OCH = CHPOCl_2$. This compound was obtained in a yield of 45 g (92% of theory) with b.p. 128° (2 mm); n_D^{20} 1.4890; d_4^{20} 1.2083.

Found %: P 12.63; 12.69; Cl 28.94; 28.82
$C_8H_{15}O_2Cl_2P$. Calculated %: P 12.65; Cl 28.97

β-Phenoxyvinylphosphinyl chloride $C_6H_5OCH = CHPOCl_2$ was synthesized by the same method as for the chlorides of β-alkoxyvinylphosphinic acids; yield 75% of theory; b.p. 131° (2 mm); n_D^{20} 1.5708; d_4^{20} 1.3710.

Found %: P 12.84; 12.89; C 40.75; 40.90; H 2.79; 2.97
$C_8H_7O_2Cl_2P$. Calculated %: P 13.08; C 40.50; 2.95

Chlorides of β-alkoxy (phenoxy)vinylphosphinic acids are also obtained in good yield by acting on the addition products ($ROCHCl-CH_2PCl_4 \cdot PCl_5$) with carboxylic acids and also with water. The chlorides of β-alkoxy(phenoxy)-vinylphosphinic acids that we studied were transparent liquids (except the solid i-$C_3H_7OCH = CHPOCl_2$), distilling in vacuum without decomposition, possessing a weak acid chloride odor and stable on keeping. All the chlorides are soluble in common organic solvents, are slowly hydrolyzed by cold water and more quickly by hot; they all decolorize bromine water.

SUMMARY

1. The addition of phosphorus pentachloride to vinyl ethers was studied.

2. A simple and convenient method was developed for synthesis of the dichlorides of β-alkoxy(phenoxy)vinylphosphinic acids.

Institute of Organic Chemistry, Academy of Sciences of the USSR Received August 23, 1953

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DIPOLE MOMENTS OF ESTERS OF ORTHOPROPIONIC AND ORTHOFORMIC ACIDS

B. A. Arbuzov and T. G. Shavsha - Tolkacheva

In previous communications we gave the dipole moments of orthocarbonic, orthosilicic and orthotitanic acids and discussed their possible structure [1]. On the basis of calculation of the dipole moments of various models of esters of orthocarbonic, orthosilicic and orthotitanic acids and of calculation of the interatomic distances of these models (allowing for the radius of action of van der Waal forces for methyl groups), we showed that the change in arrangement of the alkoxy groups of esters of orthocarbonic, orthosilicic and orthotitanic acids and the possibility of free rotation or restricted oscillation may be governed by a difference in the covalent radii of the central atom.

Continuing our studies of the dipole moments of esters of ortho acids, it appeared of interest to measure the dipole moments of esters of orthopropionic and orthoformic acids. Measurements were made of the moments of the esters set forth in Table 1.

TABLE 1

Formula of compound	Dipole moment in D
$CH_3CH_2C(OC_2H_5)_3$	1,93
$CH_3CH_2C(OC_3H_7)_3$-n	1,92
$CH_3CH_2C(OC_4H_9)_3$-n	1,84
$CH_3CH_2C(OC_5H_{11})_3$	1,90
$CH_3CH_2C)OC_8H_{17})_3$	2,00
$HC(OCH_3)_3$	1,88
$HC(OC_2H_5)_3$	1,90
$HC(OC_3H_7)_3$-n	1,92

Measurements of the moments of esters of orthopropionic acid gave values of 1,84 to 2,00 D and a mean value of 1,92 D. The mean value for the dipole moments of esters of orthoformic acid was 1,90 D. As we see, the dipole moments of esters of orthopropionic and orthoformic acids are considerably higher than those of esters of orthocarbonic acid (1,1 D).

Esters of orthopropionic and orthoformic acid possess a tetrahedral structure of the central grouping. In the distribution of the dipole moments of the individual bonds, the esters of orthopropionic acid are similar to esters of phosphorous acid since the dipole moment of the C—C bond is assumed to be zero; the distribution of the dipole moments of the individual bonds in esters of orthoformic acid is similar to the distribution of the dipole moments of the individual bonds in esters of phosphorous acid since the dipole moment of the C—H bond is assumed to be 0,4 D. Esters of orthopropionic and orthoformic acids contain three irregular alkoxy groups which make an angle of 110° with the direction of the C—O bond.

In calculating the dipole moments of molecular models of esters of orthopropionic and orthoformic acids, we assumed the dipole moment of the R→O bond to be 1,12 D, that of the C→O bond 0,9 D, and that of the H→C bond 0,4 D [2]. The valence angle of oxygen is 110°; that of the carbon 109° 30'. The dipole moment of the molecule of orthopropionic esters, calculated on the assumption of completely free rotation of the three OR groups around the C—O bonds, is 1,96 D and is almost identical with the experimentally determined value (1,92 D).

Calculation of the interatomic distances of molecular models, making allowance for the covalent radius of carbon and the radius of the fields of action of the van der Waals forces for the methyl group (2,0 A), shows that completely free rotation of the OR groups round the C—O bonds is impossible in esters of orthopropionic acid due to the considerable influence of the fields of action of van der Waals forces in all positions taken up during free rotation of the OR groups round the C—O bonds. The interatomic distance of C—O is 1,43 A.

We studied the dipole moments and interatomic distances of all possible models with synchronous movement of three OR groups together, and of the fourth OR group rotating independently, also of models with pairwise disposition of two OR groups in one plane and of a third OR group and the $C-CH_3-CH_3$ in another plane perpendicular to the first. However, among all these models we failed to find one whose dipole moment approximated to the experimentally found value; nor could we find one which reproduced the van der Waals fields of force of the methyl and methylene groups. The smallest area of superposition of the van der Waals fields of force of the methyl and methylene groups is exhibited by the rigid model A (Fig. 1), but its dipole moment is 1,15 D and very different from the experimental value.

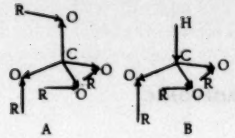

Fig. 1 Fig. 2

Esters of orthoformic acid have a dipole moment with a mean value of the order of 1,90 D. The dipole moment of the molecule of an ester of orthoformic acid with tetrahedral distribution of three C–O bonds and one C–H bond and free rotation of the three R–O groups round the C–O bonds proved to be 1,86 D and barely different from the experimental magnitude (1,90 D). Esters of orthoformic acid differ from esters of orthopropionic acid in that the former contain a C–H bond in place of a hydrocarbon chain. The radius of action of the van der Waals forces for the hydrogen atom is taken to be 1,2 A [3].

We have studied the dipole moments and interatomic distances of molecular models developed on rotation of the OR groups around the C–O bonds and we found that the free rotation of OR groups around the C–O bonds in esters of orthoformic acid is also impossible due to the considerable influence of the van der Waals fields of force of the methyl and methylene groups and of the field of action of the van der Waals forces of the hydrogen atom.

Consideration of the dipole moments and interatomic distances of rigid models of esters of orthoformic acid, when three OR groups are rotating synchronously round the C–O bonds, shows that none of these models can be accepted for the esters of orthoformic acid since they are all greatly influenced by the fields of action of the van der Waals forces of the methyl group and the hydrogen atom. A study of the dipole moments and interatomic distances of models with synchronization of movement of two OR groups in one plane and with a third OR group in the plane of the C–H bond shows that model B (Fig. 2) has the least area of superposition of the spheres of action of the van der Waals forces of the methyl groups and the hydrogen atom. However, the dipole moment of this model is 1,16 D, 0,74 D less than the experimentally found magnitude.

Consequently, nowithstanding that the mean magnitude of the dipole moment for esters of orthopropionic and orthoformic acids nearly exactly corresponds to the dipole moment of a molecule in which allowance is made for free rotation of three OR groups round the C–O bonds, on the basis of a study of the interatomic distances of models of esters we arrive at the conclusion that rotation of the OR groups round the C–O bonds is impossible in esters of orthopropionic and orthoformic acids.

A study of models with synchronization of the movement of three alkoxy groups or paired synchronized movement of the alkoxy groups in two directions perpendicular to each other likewise did not enable us to clarify the character of the possible oscillations of the OR groups in esters of orthopropionic and orthoformic acids if we assume a radius of action of 2,0 A for the van der Waals fields of force of the methyl and methylene groups and a radius of 1,2 A for the field of force of the hydrogen atom. It is most probable that the OR groups and the CH_3CH_2C chain in esters of orthopropionic acid are arranged pairwise in two planes perpendiculat to each other (model A, Fig. 1); for esters of orthoformic acid the most probable are model B (Fig. 2) and a model in which three OR groups are arranged in a plane perpendicular to the plane of the C–H bond. A model with pairwise disposition of the lakoxy groups in two planes perpendicular to each other has been proposed for esters of orthopropionic acid by one of us and Yuldasheva on the basis of measurements of the parachors of esters of orthopropionic acid [4].

Recently we measured the dipole moments of $Sb(OC_2H_5)_3$, $W(OC_6H_5)_6$ and $W(OC_6H_4CH_3)_6$. The dipole moments of these compounds were found to be 2,29, 2,13 and 2,07 D respectively. These compounds contain 5 and 6 irregular OC_2H_5, OC_6H_5 and $OC_6H_4CH_3$ groups and have a symmetrical structure. Their probable structure is a model of a bipyramid with an equilateral triangle for $Sb(OC_2H_5)_3$ and a rectangle for $W(OC_6H_5)_6$ and $W(OC_6H_4CH_3)_6$ at the base. Considering the possible models for these compounds, it can be stated that the model of the bipyramid leads to mutual compensation of the dipole moments of the Sb–O and W–O bonds, and the dipole moments of these compounds is governed only by the disposition and number of irregular groups. This condition permitted us to calculate the dipole moments of the rigid structures and of the model with free rotation of the irregular groups for these esters since the dipole moments of the Sb–O and W–O bonds are unknown.

The dipole moment of the model of the trigonal bipyramid of $Sb(OC_2H_5)_3$, for the condition of perfectly free rotation of the ethoxy groups round the respective Sb–O bonds, was calculated from the formula of Svirbely and Lander [5] and is equal to 2,19 D, which is close to the experimental value of 2,29 D. The dipole moment of the model of the tetragonal bipyramid of $W(OC_6H_5)_6$, for the condition of completely free rotation of the six irregular phenoxy groups round the respective W–O bonds, was found by the formula of Svirbely and Lander [5] to be 2,45 D, or 0,32 D more than the experimental value of 2,12 D. The dipole moment of the model of $W(OC_6H_4CH_3)_6$, for the condition of fully free rotation of the six $OC_6H_4CH_3$ groups round the W–O bonds, is 2,93 D or 0,8 D higher than the experimental value.

We made the following assumptions in our calculations of the dipole moments of the molecular models: dipole moment of the O–C_2H_5 bond 1,12 D; that of the O–C_6H_5 bond 1,0 D; that of the O–$C_6H_4CH_3$ bond 1,20 D; the corresponding data were calculated from the dipole moment of diphenyl ether, equal to 1,14 D, and the dipole moment of $(C_6H_4CH_3)_2O$ equal to 1,38 D [6]. The O–C–O angle is 110°. However, the calculated interatomic distances of the models possible with free rotation of the irregular groups, allowing for the covalent radius of antimony (1,40 A) and the covalent radius of tungsten (1,39 A) and the effective thickness of the aromatic molecule of 3,7 A [3], shows that completely free rotation of the irregular groups in the compounds $Sb(OC_2H_5)_5$ and $W(OC_6H_5)_6$ is impossible due to steric hindrance between the ethoxyl groups and the aromatic rings.

The least influence of the effective thickness of the aromatic ring and of the spheres of action of the van der Waals forces is attained when the aromatic ring is arranged in the plane of the rectangular base of the tetragonal bipyramide while the ethoxy group is arranged in the plane of the triangular base of the trigonal bipyramid. The dipole moment of $Sb(OC_2H_5)_5$ is then governed only by the disposition of the two dipole moments of the $-OC_2H_5$ bonds, since the dipole moments of the three O–C_2H_5 bonds in the plane of the triangular base of the bipyramid are mutually compensated and are equal to zero if the d pole moments of these groups are directed to different sides, or equal to 2,10 D if the dipole moments of two O–C_2H_5 bonds are directed to the same side.

In the molecules of $W(OC_6H_5)_6$ and $W(OC_6H_4CH_3)_6$ the dipole moments of four irregular groups, distributed in the plane of the rectangular base of the bipyramid, are also mutually compensated and the resultant dipole moment of $W(OC_6H_5)_6$ and $W(OC_6H_4CH_3)_6$ is equal to zero if the dipole moments of the O–C_6H_5 and O–$C_6H_4CH_3$ bonds are oppositely directed, or equal to 1,88 and 2,26 D respectively if the dipole moments of these bonds are directed to one side. The dipole moment of $Sb(O\text{-}C_2H_5)_5$ allowing for the free rotation of two O–C_2H_5 groups, is 1,50 D; for $W(OC_6H_5)_6$ it is 1,33 D; for $W(O\text{-}C_6H_4CH_3)_6$ it is 1,59 D.

The dipole moment of the model with the greatest superposition of the spheres of action of the van der Waals forces is 2,88 D for $Sb(OC_6H_5)_5$ and 3,76 D for $W(OC_6H_5)_6$.

Consequently the experimentally found dipole moments of $Sb(OC_2H_5)_5$ (2,29 D), of $W(OC_6H_5)_6$ (2,13 D) and of $W(OC_6H_4CH_3)_6$ (2,10 D) do not correspond either to the maximum or the minimum value of the dipole moments calculated for the various models. The dipole moments of molecules least affected by the spheres of action of the van der Waals forces [$Sb(OC_2H_5)_5$ 1,50 D; $W(OC_6H_5)_6$ 1,33 D; and $W(OC_6H_4CH_3)_6$ 1,59 D] differ considerably from the respective experimental values of 2,29, 2,13, and 2,10 D.

EXPERIMENTAL

The dielectric constants and densities of benzene solutions of esters of orthopropionic and orthoformic acids were determined at 25°. Dipole moments were calculated from the formula:

$$\mu = 0{,}0127 \cdot 10^{-18} \sqrt{(P_\infty - P_{el} - P_{at}) \cdot 298},$$

where MR = P_{el}; $P_{at} = 5\%\ P_{el}$.

We prepared the esters of orthopropionic acid by the transesterification of ethyl orthopropionate [4] with the appropriate alcohol in presence of conc. phosphoric acid. They had the following constants (Table 2).

TABLE 2

Formula of compound	B.p. in °C (p in mm mercury column)	n_D^{25}	d_4^{25}	MR	
				calculated	found
$CH_3CH_2C(OC_2H_5)_3$	60 (17)	1,3987	0,8826	48,69	48,30
$CH_3CH_2C(OC_3H_7)$-n	92,5–93 (14)	1,4100	0,8831	62,54	61,24
$CH_3CH_2C(OC_4H_9)_3$-n	117–117,5 (5 mm)	1,4208	0,8699	76,40	75,80
$CH_3CH_2C(OC_5H_{11})_3$	172–173,5 (4)	1,4329	0,8668	104,1	103,4
$CH_3CH_2C(OC_6H_{13})_3$	215–218 (3)	1,4404	0,8635	131,8	131,0

The methyl ester of orthoformic acid was synthesized by reaction of sodium methoxide with chloroform in ethereal solution. The ethyl ester of orthoformic acid was obtained by reacting sodium ethoxide with chloroform, while cooling, in alcoholic solution [7]. The butyl ester of orthoformic acid was obtained by transesterification of the ethyl ester with n-butyl alcohol in presence of phosphoric acid. The orthofumaric esters had the constants set forth in Table 3.

Antimony pentaethoxide with b.p. 160–162° (4–5 mm) was prepared by interaction of sodium ethoxide and antimony pentachloride in benzene [8].

TABLE 3

Formula of compound	B.p. in °C (p in mm mercury column)	d_4^{25}	n_D^{25}	MR	
				calculated	found
$(CH_3O)_3CH$	99–99.5	0.9645	1.3795	26.60	26.45
$(C_2H_5O)_3CH$	145–146	0.8870	1.3909	39.44	39.69
$(C_4H_9O)_3CH$-n	112–113 (6)	0.8726	1.4187	67.16	67.17

Tungsten hexaphenoxide [9] with m.p. 98° was prepared by interaction of tungsten hexachloride with 10 parts by weight of phenol. The precipitate was washed with alcohol and recrystallized from alcohol. Dark-red needles and leaflets melting at 98°.

WO_3. Calculated 0.02319 g
WO_3. Found 0.02320 g

Hexa(p-Tolyloxy) tungsten with m.p. 134-135° was prepared by reaction of 25 g p-cresol with 3 g tungsten hexachloride. Hydrogen chloride started to come off in the cold. The reaction mixture was heated to the boil for 10-15 min. and gave a dark, cherry-red solution. Addition of a small quantity of absolute alcohol followed by standing overnight at 0° resulted in deposition of black crystals which were drained, washed on the filter with absolute alcohol; yield 2.7 g. After recrystallization from absolute alcohol in a Soxhlet apparatus, black crystals with m.p. 130-131° were obtained. The black residue on the filter was extracted with boiling benzene; to the benzene solution was added an equal volume of alcohol. After a short time, black crystals came down. Recrystallization from a large quantity of benzene gave needles with a dark garnet color, m.p. 134-135°.

WO_3. Calculated 0.008864 g
WO_3. Found 0.0088 g

The dielectric constants, densities and polarizations of benzene solutions of various concentrations of the compounds at 25° are set forth in Tables 4 to 14.

TABLE 4

$CH_3CH_2C(OC_2H_5)_3$

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.006011	2.2861	0.8730	27.00	116.4
0.003364	2.2833	0.8725	26.93	123.3
0.007904	2.2970	0.8725	27.28	113.0
0.008967	2.2982	0.8725	27.35	108.5
0.010820	2.3029	0.8725	27.48	107.1
0.013280	2.3096	0.8725	27.66	106.1

P_∞ = 128.0; $P_A + E$ = 50.7
P_{or} = 77.3; μ = 1.93D

TABLE 5

$CH_3CH_2C(OC_3H_7)_3$-n

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.004453	2.2913	0.8742	27.10	138.2
0.006032	2.2974	0.8742	27.26	136.2
0.007147	2.3008	0.8742	27.26	134.9
0.010150	2.3101	0.8742	27.64	130.9
0.011660	2.3166	0.8742	27.84	131.3
0.010910	2.3130	0.8742	27.73	130.4

P_∞ = 141.0; $P_A + E$ = 64.30
P_{or} = 76.70; μ = 1.92D

TABLE 6

$CH_3CH_2C(OC_4H_9)_3$-n

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.001843	2.2789	0.8740	26.80	142.1
0.002102	2.2790	0.8740	26.85	141.9
0.005449	2.2852	0.8740	27.16	125.7
0.003961	2.2831	0.8740	27.02	132.4
0.006794	2.2902	0.8740	27.29	129.5
0.004172	2.2847	0.8740	27.05	137.0

P_∞ = 150.0; $P_A + E$ = 79.5;
P_{or} = 70.5; μ = 1.84 D

TABLE 7

$CH_3CH_2C(OC_6H_{13})_3$

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.002816	2.2850	0.8746	27.04	183.2
0.004553	2.2885	0.8746	27.18	170.5
0.005591	2.2918	0.8746	27.41	169.5
0.006276	2.2931	0.8746	27.48	166.3
0.007104	2.2943	0.8746	27.57	162.6
0.007975	2.2975	0.8746	27.70	163.4

P_∞ = 184.0; $P_A + E$ = 108.6;
P_{or} = 75.4; μ = 1.90 D

TABLE 8

$CH_3CH_2C(OC_2H_{17})_3$

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,002116	2,2804	0,8734	27,02	215,6
0,002602	2,2821	0,8736	27,09	213,0
0,003980	2,2865	0,8734	27,34	209,9
0,003131	2,2830	0,8734	27,34	207,3
0,005117	2,2880	0,8734	27,48	198,9
0,005856	2,2904	0,8734	27,59	197,0

$P_\infty = 221,0$; $P_{A+E} = 137,6$;
$P_{or} = 83,4$; $\mu = 2,00$ D

TABLE 9

$HC(OCH_3)_3$

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,004101	2,2887	0,8735	26,91	98,04
0,008074	2,3014	0,8742	27,11	87,38
0,012610	2,3120	0,8749	27,29	79,58
0,015600	2,3324	0,8751	27,62	89,77
0,026360	2,3665	0,8768	28,87	85,36
0,021400	2,3521	0,8764	27,90	86,45

$P_\infty = 100,0$; $P_{A+E} = 26,72$;
$P_{or} = 73,28$; $\mu = 1,88$ D

TABLE 10

$HC(OC_2H_5)_3$

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,002999	2,2848	0,8730	26,92	120,2
0,005883	2,2962	0,8730	27,14	114,1
0,008883	2,3088	0,8730	27,39	114,4
0,012150	2,3211	0,8730	27,65	110,4
0,01520	2,3330	0,8730	27,91	111,0
0,01753	2,3415	0,8730	28,08	110,0

$P_\infty = 117,0$; $P_{A+E} = 41,67$;
$P_{or} = 75,33$; $\mu = 1,90$ D

TABLE 11

$HC(OC_4H_9)_3$

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,002468	2,2840	0,8728	26,96	149,0
0,004551	2,2924	0,8728	27,19	137,6
0,006772	2,3022	0,8728	27,45	142,9
0,008849	2,3114	0,8728	27,69	143,6
0,012040	2,3232	0,8728	28,04	141,5
0,010680	2,3185	0,8728	27,88	141,3

$P_\infty = 147,00$; $P_{A+E} = 70,53$
$P_{or} = 76,47$; $\mu = 1,92$ D

TABLE 12

$Sb(OC_2H_5)_3$

C_2	ϵ_{12}	d_{12}	n_D^{25}	MR_{12}	MR_2	P_{12}	P_2
0,002558	2,2929	0,8783	1,4959	26,20	70,22	27,02	189,9
0,003238	2,2980	0,8793	1,4960	26,25	71,09	27,11	181,0
0,004887	2,3058	0,8819	1,4960	26,32	71,00	27,31	170,3
0,003566	2,3091	0,8805	1,4959	26,25	65,85	27,29	217,2
0,005983	2,3162	0,8838	1,4959	26,35	69,40	27,50	177,7
0,007346	2,3302	0,0059	1,4958	26,43	69,19	27,72	176,9

$P_\infty = 185,0$; $P_{A+E} = 75,60$; $P_{or} = 109,4$; $\mu = 2,29$ D; $P_{el} = 72,0$

TABLE 13

$W(OC_6H_5)_6$

C_2	ϵ_{12}	d_{12}	n_D^{25}	MR_{12}	MR_2	P_{12}	P_2
0,00048	2,2754	0,8755	1,4961	26,18	191,0	26,75	278,5
0,00087	2,2799	0,8767	1,4976	26,29	254,4	26,84	305,9
0,00135	2,2817	0,8784	1,4985	26,34	247,7	26,92	272,1
0,001530	2,2840	0,8798	1,4991	26,44	234,4	26,99	260,9
0,00061	2,2765	0,8774	1,4968	26,19	194,1	26,73	235,4

$P_\infty = 283,00$; $P_{A+E} = 189,00$; $P_{or} = 94,00$; $\mu = 2,13$ D; $P_{el} = 180,0$

TABLE 14

$W(OC_6H_4CH_3)_6$

C_2	ϵ_{12}	d_{12}	n_D^{20}	MR_{12}	MR_2	P_{12}	P_2
0.00033	2.2738	0.8755	1.4953	26.12	98.79	26.67	254.8
0.00071	2.2788	0.8768	1.4968	26.24	234.1	26.84	317.0
0.00090	2.2797	0.8774	1.4967	26.26	212.5	26.87	303.3
0.001116	2.2819	0.8784	1.4977	26.34	242.0	26.92	301.6
0.001322	2.2842	0.8786	1.4984	26.40	262.5	26.98	315.6
0.0005	2.2769	0.8746	1.4963	26.22	300.5	26.79	397.7

$P_\infty = 310.0$; $P_{A+E} = 218.4$; $P_{or} = 91.6$; $\mu = 2.10$ D; $P_{el} = 208.0$

SUMMARY

1. Measurements were made of the dipole moments of ethyl, n-propyl, n-butyl, hexyl and octyl esters of orthopropionic acid (mean value of dipole moment 1.92 D), and of the methyl, ethyl and n-butyl esters of orthoformic acid (mean value 1.90 D).

2. Measurements were made of the dipole moments and refractivities of antimony pentaethoxide (2.29 D), tungsten hexaphenoxide (2.13 D) and hexa-p-tolyloxytungsten (2.10 D).

3. Calculation of the interatomic distances of various molecular models, allowing for the radius of the spheres of action of the van der Waals forces of the methyl and methylene groups (2.0 A) and the radius of the spheres of action of the van der Waals forces of the hydrogen atom (1.2 A), shows that free rotation of the irregular groups is impossible in these compounds.

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Received June 25, 1953

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PARACHORS OF MONOESTERS OF ETHYLPHOSPHONOUS ACID

B. A. Arbuzov and V. S. Vinogradova

As was shown in previous communications, the structural peculiarities of certain types of organic molecules, characterized by the presence of a certain spatial distribution of long hydrocarbon chains, can be readily detected from the magnitudes of the parachors. On calculating the theoretical values of the parachors by the method of "group values", these peculiarities of structure are manifested in corrections for bending and parallelity of the chains and the value of the molecular parachor is reduced.

A current problem of great interest which has not been adequately clarified is that of the nature and causes of appearance of corrections for parallelity. Up to now we have studied the parachors of compounds in which the fall of molecular parachor was brought about by interaction between the carbon atoms of two or three chains inside one molecule and by the corresponding distribution of the chains parallel to one another.

Interesting examples, in which the possibility of intramolecular reaction of chains is excluded, are the monoesters of ethylphosphonous acid. The monoesters of ethylphosphonous acid are analogs of dialkylphosphorous acids in which one hydrocarbon chain is directly attached to phosphorus. Study of their parachors is therefore of interest because of the possibility of establishing whether or not they associate. Association occurs in certain dialkylphosphorous and phosphonous acids [1].

In this communication we present our data for the parachors of a series of monoesters of ethylphosphonous acid, synthesized by Rizpolozhensky [2]; their constants are set forth in Table 1.

TABLE 1

Formula	B.p. in °C (p in mm mercury column)		d_4^{20}	n_D^{20}	γ^{20}
CH_3	65–66	(11)	1,0795	1,4273	34,5
C_2H_5	68–69	(9)	1,0195	1,4242	30,8
n-C_3H_7	80	(9)	0,9866	1,4285	28,8
i-C_3H_7	69,5–70	(10)	0,9820	1,4233	27,7
n-C_4H_9	68	(1,5)	0,9753	1,4340	29,5
i-C_4H_9	86,5–87	(8)	0,9688	1,4300	28,1
C_6H_{13}	87,5–88	(1,5)	0,9507	1,4374	29,4
C_7H_{15}	102	(3,5)	0,9383	1,4395	29,1
C_8H_{17}	102,5–103	(1)	0,9316	1,4440	29,1
C_9H_{19}	122–123	(3,5)	0,9216	1,4430	29,4

In Table 2 are set forth the theoretical values of the parachors calculated for the monomeric form of the monoesters of ethylphosphonous acid with allowance for the β-correction for the bending of the ester chain (1,4 unit) ([P] calc. I). The group value of $C_2H_5P\begin{matrix}O(C)\\ \diagdown\\ \diagup\\ OH\end{matrix}$ = 187,0 units was calculated by the usual method from the parachor of the methyl ester (a correction for the β-carbon of the ethyl chain of −2,0 units [3] enters into the group value).

As we see from Table 2, the experimental parachors have lower values than the theoretical values $[P]_{calc.}$ I. The obtained deviations, which exceed the experimental error, cannot be accounted for by inadequate purity of the investigated compounds. Repeated syntheses and purification did not appreciably change the values of the parachors. Evidently in this case the low values of the parachors must be explained by the presence of structural factors which were not allowed for in the corrections introduced. Low parachor values were obtained for esters of fumaric acid [4] in which we can hardly suggest that possibility of parallel arrangement of chains in view of the trans-position of the carboxyl groups; the same phenomenon has been observed with esters of terephthalic acid [5]

and a number of other acids in which intramolecular interaction of chains is likewise highly improbable.

The compared values of calculated and found parachors for esters of fumaric and terephthalic acids were obtained on the assumption of a structure with parallel chains of different molecules and therefore with introduction of a correction in the value of the molecular parachor of −1.1 unit (1/2 ‖) per carbon atom of the ester chain at the β-carbon.

The parachors of monoesters of ethylphosphonous acid, calculated with a correction for bending (β = −1.4 unit) and a correction for parallelity of the ester chains of different molecules (1/2 ‖), are set forth in Table 2 [$P]_{calc.}$ II. Regarding esters of isostructure in Table 2, the corrections for bending in the isopropyl ester and for parallelity in the isobutyl ester of ethylphosphonous acid are assumed both for the main and the side chain*. As we see from the data of Table 2, the adoption of corrections for parallelity of the ester chains of two molecules leads to good agreement between the experimental and calculated parachors.

A second interesting problem concerns the possibility of the occurrence of association in monoesters of ethylphosphonous acids. From data for Raman spectra of lower dialkylphosphorous acids from dimethyl through dibutylphosphorous acids, A. E. Arbuzov, Batuev and Vinogradova [1] inferred the occurrence of association due to hydrogen bonding. Subsequently we arrived at the conclusion [6], on the basis of a study of the parachors of dialkylphosphorous acids, that the lower dialkylphosphorous acids were associated. The higher dialkylphosphorous acids, starting from dihexylphosphorous acid, proved to be monomeric. Association of dialkylphosphorous acids due to hydrogen bonds was confirmed by Meyrick and Thomson [7] by a study of the Raman and infrared spectra of dimethyl-, diethyl- and diisopropylphosphorous acids. Later, however, Bellamy and Beecher [8] did not confirm the data of Meyrick and Thomson for the infrared spectrum of diethylphosphorous acid.

We carried out [9] a cryoscopic measurement of the molecular weights of the dialkylphosphorous acids in benzene and showed that with increasing concentration the molecular weight of dimethylphosphorous acid rises, which indicates that dimethylphosphorous acid is associated in the liquid state [9]. Kosolapoff and Powell [10] point out that our data on rising molecular weights of lower dialkyphosphorous acids with increasing concentration were obtained for unusually high concentrations; on the basis of molecular weight determinations of diethyl and dibutyl- phosphorous acids in dilute solution, they consider them to be monomeric. Di-(p-di-methylaminophenyl) phosphorous acid was also found to be monomeric. Kosolapoff and McCullough [11] attempted to determine the susceptibility of dialkylphosphorous acids to hydrogen bond formation from their heats of mixing with chloroform.

TABLE 2

$C_2H_5P(OR)(OH)$	$[P]_{found}$	$[P]_{calc.}$ I β-correction	Deviation, in %	$[P]_{calc.}$ II	Correction	Deviation in %
CH_3	242.8	242.8	0	242.8	—	0
C_2H_5	282.0	281.0	+ 0.4	281.0	−1.4 β	+ 0.4
n-C_3H_7	319.5	321.0	− 0.4	319.9	−2.5 β 1/2 ‖	− 0.1
i-C_3H_7	318.2	317.0	+ 0.4	317.0	−2.8 2β	+ 0.4
n-C_4H_9	359.6	361.1	− 0.4	358.8	−3.6 β 1/2 ‖ ·2	+ 0.2
i-C_4H_9	356.0	358.4	− 0.7	356.2	−3.6 β 1/2 ‖ ·2	0
C_6H_{13}	436.5	441.2	− 1.1	436.8	−5.8 β 1/2 ‖ ·4	0
C_7H_{15}	475.8	481.4	− 1.1	475.9	−6.9 β 1/2 ‖ ·5	0
C_8H_{17}	514.1	521.6	− 1.4	515.0	−8.0 β 1/2 ‖ ·6	− 0.1
C_9H_{19}	553.7	561.8	− 1.4	554.1	−9.1 β 1/2 ‖ ·7	0

We obtained data for the molecular weights of dialkylphosphorous acids both for low and unusually high concentrations. In the case of high concentrations these data must be considered carefully and should be regarded as evidence of only a tendency to increase of molecular weight. It must be pointed out that for associated liquids in a solvent (dioxan) which breaks the hydrogen bond of the investigated substances, the molecular weight does not rise appreciabley even up to a concentration of 8-9 moles per 100 moles solvent (acetic acid in dioxane [12].

It follows from what has been said that the problem of the association of dialkylphosphorous acids and closely related types of organic derivatives of phosphorus in the liquid state cannot be regarded as conclusively solved. For this reason, interest attaches to the study of the presence or absence of association in acid esters of ethylphosphonous

* The question of the need for corrections for the side chain cannot be said to be finally settled.

acid, since, in the opinion of Kosolapoff [11], substitution of the RO group by R directly linked to the phosphorus must increase the susceptibility to formation of a hydrogen bond.

In work with fatty acids Gibling [13] established the influence of association upon the magnitude of the molecular parachor. For higher fatty acids, associated to dimeric complexes, the difference in the value of the parachor, for each CH_2 group (Δ_{CH_2}) considerably exceeds the usual difference of 39.8 units. We carried out calculations of this type for the investigated esters, introducing corrections for interaction and without corrections. The difference obtained when corrections are introduced does not permit us to judge whether association of monoesters of ethylphosphonous acid occurs.

It is interesting to note that the group value of , calculated with corrections from the parachors of the nonyl and octyl esters (186.6 units), is very close to the value obtained from the parachor of the methyl ester. This also indicates the great probability of a monomeric form for esters of ethylphosphonous acid. The parachors calculated on the assumption of a dimeric form of the first members of the series, in the same way as for the dialkylphosphorous acids, do not give any indications of association of esters of ethylphosphonous acid.

We supplemented our data for the parachors of the monoesters of ethylphosphonous acid by carrying out cryoscopic measurements. In Table 3 are set forth the molecular weights determined in benzene solutions of various concentrations.

TABLE 3

theor. mol.wt.	Concentration (mole %)	Mol. wt. found	mol. wt. theor.	Concentration (mole %)	Mol. wt. found
C_2H_5 122.1	0.37	122.4	C_6H_{15} 178.2	0.27	181.6
	1.38	127.5		0.90	189.4
	2.06	129.7		1.67	194.5
	2.83	133.2		2.48	199.0
	4.41	135.7		3.77	199.8
n-C_3H_7 136.1	0.35	139.2	C_7H_{17} 192.2		
	1.18	144.9		0.36	190.4
	1.74	148.1		0.97	197.5
	2.60	151.2		1.95	198.9
	3.39	152.0		2.72	197.5
	4.65	153.8		3.34	197.6
n-C_4H_9 150.1	0.34	150.6	C_8H_{17} 206.2	0.16	203.4
	0.91	150.4		0.45	204.9
	2.27	155.4		0.93	211.5
	3.38	157.4		1.45	217.4
				2.15	221.2
				2.91	223.3
i-C_4H_9 150.1	0.31	150.0		3.58	220.7
	1.00	155.1			
	2.13	156.9	C_9H_{19} 220.3	0.26	221.4
	2.98	158.9		0.87	225.3
				0.93	227.0

As we see from Table 3, with rising concentration of the benzene solutions, in nearly all cases an insignificant rise of molecular weight is observed, not exceeding 10% of the monomeric molecular weight even at concentrations of 3-4 mole-%. However, on the basis of these data it is impossible to draw final conclusions about the absence of association in the lower monoesters of ethylphosphonous acid in the liquid state.

SUMMARY

1. Parachors of the series of monoesters of ethylphosphonous acid from methyl through nonyl have been found. There is good agreement between found and calculated parachors on the assumption of interaction of the chains of different molecules.

2. Data for parachors and molecular weights, the latter determined cryoscopically in benzene, point to monomeric forms of the esters examined rather than to their association.

Received June 19, 1953

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PARACHORS OF SOME ESTERS OF 5-NONANOL

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The method of group values proposed by Gibling [1] for calculation of the molecular parachor provides evidence of interaction of hydrocarbon chains of ester groups in esters of organic and inorganic acids, amines and other types of organic compounds both with the central atoms ("bending correction") and with one another ("correction for parallelity"). In the majority of compounds studied by the method of parachors, interaction of chains inside a molecule has been found, although recent parachor studies have given indications of interaction between the hydrocarbon chains of different molecules [2].

In applying the parachor method to the elucidation of structures of organic compounds, an unclarified aspect has been the corrections to be applied to molecular parachor values of compounds containing iso radicals. At the same time, branching of hydrocarbon radicals may exercise a considerable influence on a series of physical properties of organic compounds as clearly demonstrated, for example, in recent studies by Bradley, Mehrotra and Wardlaw [3] on alkoxyl derivatives of silicon, titanium and zirconium. Bradley Mehrotra and Wardlau reach the conclusion that there is strong intermolecular interaction of the alkyl groups in these compounds.

In calculating the parachors of iso compounds with allowance for parallelity we may start from the consideration that either only the main chains interact with one another or there is also interaction with the side chains. A similar alternative may be considered in relation to the correction for chain bending. For esters of carbonic, malonic [1] and sulfurous acids [4] with branched chains, Gibling only applies a parallelity correction for the main chains.

In previous communications we presented calculations of the parachors of a series of iso esters with introduction of corrections for interaction between carbon atoms of both the main and the side chains. Misprints appeared in a table setting forth the calculated parachors of these esters with allowance for interaction also of the side chains [5]. We therefore reproduce this table again in Table 1 with the modification that the parachors of the isobutyl and isoamyl esters of malonic acid are calculated on the basis of a group value of (C)OC$\overset{O}{\overset{\|}{C}}H_2C\overset{O}{\overset{\|}{C}}$O(C) 173.5 units, which value was found from the methyl ester with introduction of a correction of −2.2 units for parallelity of the carbons of the methyl groups.

As we see from Table 1, the data do not provide an answer to the question of the need to introduce corrections for the side chain, since no sharp difference in corrections is observed. In the majority of cases, however, the best results are got by introducing corrections for the side chain. Comparison of the parachors obtained for isopropyl phosphite [6] and isopropyl phosphate [5] with the parachors calculated with insertion of corrections for bending of all the β-carbon atoms of the ester chains showed good agreement.

On the assumption of parallelity of the two ester chains in esters of phosphorous acids [7], we calculated the parachor of triisobutyl phosphite:

	$[P]_{found}$	$[P]_{calc.}$	Deviation in %	Corrections
i-$(C_4H_9O)_3P$	610.2	612.4	− 0.3	− 8.63 β 2 ‖
		614.7	− 0.7	− 6.43 β 1 ‖

The data obtained also indicate the necessity to insert corrections for parallelity of the carbons of both the main and the side chains.

Gibling [4] derives the parachor of triisobutyl phosphate but does not apply corrections for branching of the ester chains; he assumes that the methyl radicals are arranged in the plane of symmetry of the PO_4 group so that corrections in this case should be of subsidiary importance. On the basis of data for ortho esters and acetals, Voronkov [8] concludes that corrections for parallelity in iso radicals need only be introduced for the main chains. Calculations of the parachors of the isopropyl and isoamyl esters of succinic and adipic acids * with allowance

* These parachors are enumerated in Vogel's paper [9].

TABLE 1

Name of compound	$[P]_{found}$	$[P]_{calc.}$	Deviation in %	Corrections
Diisobutyl carbonate	428.1	426.9	+ 0.3	− 4.4 2 ‖
		429.1	− 0.2	− 2.2 1 ‖
Diisoamyl carbonate	505.0	505.0	0	− 6.6 3 ‖
		507.2	− 0.4	− 4.4 2 ‖
Diisobutyl malonate*	511.8	511.3	0	− 8.8 4 ‖
		513.5	− 0.3	− 6.6 3 ‖
Diisoamyl malonate*	586.9	589.2	− 0.3	− 11.0 5 ‖
		591.4	− 0.7	− 8.8 4 ‖
Diisobutyl sulfite	450.6	449.0	+ 0.3	− 6.0 2 β; 2 ‖
		451.2	− 0.1	− 3.8 2 β; 1 ‖
Diisoamyl sulfite **	525.7	527.1	− 0.2	− 8.2 2 β; 3 ‖
		529.3	− 0.7	− 6.0 2 β; 3 ‖

* In paper [5] this was wrongly printed as diisoamyl sulfite.
** In the same paper this was printed as diisoamyl sulfate.

TABLE 2

Name of compound	$[P]_{found}$	$[P]_{calc.}$	Deviations (%)	Corrections
5-Nonyl acetate	491.2	493.1	− 0.3	− 1.4 2 δ
5-Nonyl carbonate	818.6	820.2	− 0.2	− 13.2 6 ‖
		826.9	− 0.8	− 6.6 3 ‖
5-Nonyl malonate	900.3	902.3	− 0.2	− 19.8 9 ‖
		911.1	− 1.2	− 11.0 5 ‖
Tetra(5-nonyl)silicate	1556.1	1566.8	− 0.6	− 46.4 8 γ 16 ‖
		1584.5	− 1.8	− 28.8 8 γ 8 ‖
Tri(5-nonyl) borate	1173.8*	1172.7	+ 0.1	− 30.4 6 γ 10 ‖
		1190.9	− 1.4	− 12.8 6 γ 2 ‖

* Calculated from γ and d_0, determined at 60°.

for parallelity of the main and side chains do not supply supplementary data. The difference in parachors in this case is 0.1-0.2% and lies within the limits of experimental error.

We see that inspection of the literature data for parachors of iso compounds does not lead to a decisive answer to the question of corrections. For the purpose of obtaining supplementary data, we synthesized esters of 5-nonanol in which the differences in corrections are large and more conspicuous. In Table 2 the data that we obtained for the parachors of 5-nonyl esters are compared with the theoretical values calculated for two possible structures: assumption of interaction of carbon atoms of only the main chains and introduction of corrections for interaction of both the main and the side chains.

Assuming a paired arrangement of ester chains in orthosilicates [10] and their branching in the 5-nonyl radical, the corrections for parallelity are taken as 4 ‖ for the δ-carbon and 4‖ for the ε-carbon for each pair of 5-nonyl chains, giving a total of 16 ‖ for the molecule of tetra(dibutylcarbinyl) silicate. The parachor of 5-nonyl borate, calculated with allowance for interaction of the side chains, includes a correction for parallelity for the δ- and ε-carbons of the two 5-nonyl chains arranged on one side of the BO_3 group (8 ‖) and for the δ- and ε-carbons of the third branched chain located on the other side of the BO_3 group (2 ‖) [11].

The data set forth in Table 2 conclusively point to the necessity for insertion of corrections for parallelity of the side chains. The errors resulting from allowance of corrections only for the main chains reach 0.8-1.5%. Parachors obtained for compounds containing branched chains are lower in the majority of cases than the parachors of their normal-chain isomers. Thus, for example, the parachor of the tetranonyl ester of orthosilicic acid is 1591.8 units [10] and differs from the parachor of tetra(5-nonyl)-silicate by 35.7 units. The difference, however, in the group values of these esters is only 10.4 units. Consequently the 25.3 units of difference in the parachors must be attributed to the corrections which are introduced to allow for the structural differences between esters with branched and unbranched chains.

EXPERIMENTAL

5-Nonanol was prepared by the method of [12] and had b.p. 88-88.5° (13 mm).

5-Nonyl carbonate was prepared by transesterification of diethyl carbonate, using 12 g 5-nonanol and 4 g ethyl carbonate. The reaction was carried out in a flask with a Widmer column in presence of metallic sodium as catalyst. Two distillations gave a pure product (4 g) with b.p. 156-156.5° (3.5 mm); n_D^{20} 1.4330; d_4^{20} 0.8765; γ^{20} 27.1 dynes/cm.

	Found %:	C 72.62; H 12.18
$C_{19}H_{38}O_3$.	Calculated %:	C 72.56; H 12.17

5-Nonyl acetate. From 10 g 5-nonanol and 5.5 g acetyl chloride was obtained 9 g 5-nonyl acetate with b.p. 206-207° (754 mm); n_D^{20} 1.4205; d_4^{20} 0.8577; γ^{20} 26.2 dynes/cm [13].

5-Nonyl malonate was obtained by transesterification of diethyl malonate (5.5 g) with 5-nonanol (10 g) in presence of metallic sodium (pellets). Ethyl alcohol came off with difficulty at a bath temperature of 80-115°. 4 ml alcohol came over. Two distillations gave 5 g product with b.p. 192-193° (7.5 mm); n_D^{20} 1.4415; d_4^{20} 0.9156; γ^{20} 28.5.

	Found %:	C 70.30; H 11.11
$C_{21}H_{40}O_4$.	Calculated %:	C 70.74; H 11.31

Tri(5-nonyl) borate. Reactants were 7 g tri-n-butyl borate and 15 g 5-nonanol. The butyl alcohol came off at a bath temperature of 180°. 7 ml of the alcohol was collected (theoretical requirement 6.6 g). The bath temperature at the close of distillation of the alcohol was 240°. Two distillations gave a rapidly crystallizing product with b.p. 167° (1.5 mm); d_4^{20} 0.8159; γ^{20} 22.33; m.p. 55-56°.

	Found %:	B 2.45
$C_{27}H_{57}O_3B$.	Calculated %:	B 2.45

Tetra(5-nonyl) silicate was prepared by transesterification of tetraethyl orthosilicate (6 g) with 5-nonanol (16 g). The reaction takes place on adding a small pellet of sodium. 5.2 ml alcohol came off (5.5 g theoretical amount) at a bath temperature of 250°. On vacuum distillation, 2 g 5-nonanol (73-75°, 5 mm) was recovered and 9 g ester was obtained with b.p. 200-201° (1 mm); n_D^{20} 1.4395; d_4^{20} 0.8718; γ^{20} 26.6.

	Found %:	C 72.06; H 12.56
$C_{36}H_{76}O_4Si$.	Calculated %:	C 71.94; H 12.74

SUMMARY

1. The 5-nonyl esters of carbonic, malonic, boric and orthosilicic acids, not previously described in the literature, were synthesized.

2. The parachors that we obtained indicate the necessity for corrections for the parallelity of the main and side chains.

Received June 19, 1953

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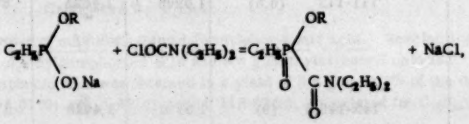
ETHYLPHOSPHONOUS ESTERS AND SOME OF THEIR TRANSFORMATIONS

COMMUNICATION 4. SYNTHESIS OF ESTERS OF ETHYLDIETHYLAMIDOFORMYLPHOSPHONIC ACID

B. A. Arbuzov and N. I. Rizpolozhensky

In the preceding paper [1] we described the synthesis of diethylamides of esters of phosphonoformic acid. In the course of study of the properties of esters of ethylphosphonous acid (full) and of partial esters of ethylphosphonous acid synthesized by us [2], we prepared a series of esters of ethyldiethylamidoformylphosphonic acid. These esters, like the diethylamides of the esters of phosphonoformic acid, were prepared by two methods. We have previously described [4] one of the methods of preparation of esters of ethyldiethylamidoformylphosphonous acid – the A. E. Arbuzov rearrangement [3] of full esters of ethylphosphonous acid with diethylcarbamyl chloride.

In the present paper we describe a synthesis of esters of ethyldiethylamidoformylphosphonic acid by the action of diethylcarbamyl chloride on the sodium salts of esters of ethylphosphonous acid [5]:



where R = C_2H_5 –; n-C_3H_7 –; i-C_3H_7 –; n-C_4H_9 –; i-C_4H_9 –;

n-C_5H_{11} –; n-C_7H_{15} –; n-C_8H_{17} –; n-C_9H_{19} –; n-$C_{10}H_{21}$ –;

It must be pointed out that the yield of esters of ethyldiethylamidoformylphosphonic acid is lower in this case than in rearrangement of the full esters of ethylphosphonous acid by diethylcarbamyl chloride.

The physical properties of the esters prepared are set forth in Table 1.

It may be noted that on examining the table of physical properties the measured molecular refraction is seen to differ from the calculated value by approximately a constant amount, 137 on the average. This indicates that for esters of the structure in question the value of the atomic refraction of nitrogen and phosphorus should have differed from the value adopted by us in calculating the molecular refraction.

For the atomic refraction of phosphorus we took the value of 4.27* [6]. For the AR of nitrogen we took 2.49 [7]. The remaining values of atomic refractions were those given by Eisenlohr.

EXPERIMENTAL

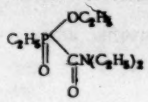
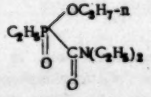
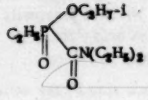
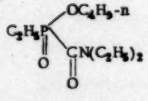
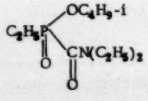
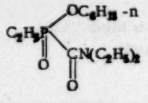
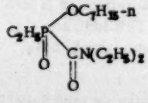
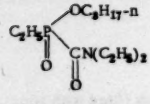
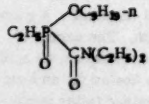
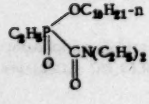
Synthesis of ethyl ester of ethyldiethylamidoformylphosphonic acid. Into a 3-necked flask fitted with stirrer, reflux condenser and dropping funnel were introduced 1 g sodium (excess of 0.3 g) and about 80 ml ether. 4 g ethyl ester of ethylphosphonous acid was then run in. The flask was heated for 2 hours on a water bath. The excess of sodium was eliminated and into the ethereal solution of the sodium salt of the ethyl ester of ethylphosphonous acid was run (through the dropping funnel) 4.3 g diethylcarbamyl chloride, after which the flask was heated for an hour on the water bath. The precipitate of sodium chloride was separated by centrifuging and the residue (after removal of the ether) was distilled in vacuum from an Arbuzov flask.

Two fractional distillations from the Arbuzov flask yielded the ethyl ester of ethyldiethylamidoformylphosphonic acid with the following constants: b.p. 107-108° (2 mm); d_4^{20} 1.0538; n_D^{20} 1.4630; found MR 57.82; calculated for $C_9H_{20}O_3PN$ MR 58.59; yield 2.9 g, or 40% of theoretical.

	Found %:	P 13.85; 13.92
$C_9H_{20}O_3PN$	Calculated %:	P 14.03

In all the following experiments the same procedure was used for the syntheses.

TABLE 1

Formula of ester	B.p. in °C (p in mm Hg column)		d_4^{20}	n_D^{20}	MR found	MR calculated	Yield in %
	107-108	(2)	1,0538	1,4630	57,82	56,59	40
	112-113	(2)	1,0346	1,4622	62,54	61,21	36,8
	133-134	(9)	1,0286	1,4595	62,58	61,21	35,1
	111-112	(0,5)	1,0208	1,4625	67,20	65,82	42,3
	145-146,5	(9)	1,0170	1,4610	67,26	65,82	45,7
	131-132	(2,5)	0,9725	1,4500	76,65	75,05	34,8
	143-145	(2)	0,9817	1,4565	80,75	79,67	30
	137-138	(0,5)	0,9782	1,4618	85,80	84,29	42
	145-147	(1,5)	0,9702	1,4612	90,38	88,91	55
	160-162	(1,5)	0,9630	1,4600	94,84	93,52	53,5

Synthesis of n-propyl ester of ethyldiethylamidoformylphosphonic acid. Reactants were 3.8 g n-propyl ester of ethylphosphonous acid, 0.7 g sodium (with excess) and 3.8 g diethylcarbamyl chloride. The ester obtained had the constants: b.p. 112-113° (2 mm); d_4^{20} 1.0346; n_D^{20} 1.4622; found MR 62.54; calculated for $C_{10}H_{22}O_3PN$ MR 61.21; yield 2.4 g, or 36.8% of theoretical.

Found %: P 13.12; 13.26

$C_{10}H_{22}O_3PN$. Calculated %: P 13.19

Synthesis of isopropyl ester of ethyldiethylamidoformylphosphonic acid. Reactants were 0.6 g sodium (with excess), 2.5 g isopropyl ester of ethylphosphonous acid and 2.5 g diethylcarbamyl chloride. The isopropyl ester of ethyldiethylamidoformylphosphonic acid had the following constants: b.p. 133-134° (9 mm); d_4^{20} 1.0286; n_D^{20} 1.4595; Found MR 62.58; calculated for $C_{10}H_{22}O_3PN$. MR 61.21; yeild of ester 1.5 g, ot 35% of the theoretical.

Found %: P 13.12; 13.00

$C_2H_{22}O_3PN$. Calculated %: P 13.19

Preparation of n-butyl ester of ethyldiethylamidoformylphosphonic acid. Reactants were 1.5 g sodium (with excess), 6.0 g butyl ester of ethylphosphonous acid, 5.4 g diethylcarbamyl chloride. The n-butyl ester of ethyldiethylamidoformylphosphonic acid had the following constants: b.p. 111-112° (0.5 mm); d_4^{20} 1.0208; n_D^{20} 1.4625; found MR 67.20; calculated for $C_{11}H_{24}O_3PN$ MR 65.82; yield 4.2 g, or 42.3% of theoretical.

Found %: P 12.41; 12.55

$C_{17}H_{24}O_3PN$. Calculated %: P 12.42

Preparation of isobutyl ester of ethyldiethylamidoformylphosphonic acid. Reactants were 1 g sodium (with excess), 4.2 g isobutyl ester of ethylphosphonous acid and 3.8 g diethylcarbamyl chloride. The isobutyl ester of ethyldiethylamidoformylphosphonic acid was obtained in a yield of 3.2 g or 45.7% of the theoretical. Constants: b.p. 145-146.5° (9 mm); d_4^{20} 1.0170; n_D^{20} 1.4610; found MR 67.26; calculated for $C_{11}H_{24}O_3PN$ MR 65.82.

Found %: P 12.25; 12.33

$C_{11}H_{24}O_3PN$. Calculated %: P 12.42

Synthesis of n-hexyl ester of ethyldiethylamidoformylphosphonic acid. Reactants were 1.4 g sodium (with excess), 7.2 g n-hexyl ester of ethylphosphonous acid and 5.5 g diethylcarbamyl chloride. The hexyl ester of ethyldiethylamidoformylphosphonic acid was obtained in the amount of 3.9 g or 34.8% of the theoretical b.p. 131-132° (2.5 mm); d_4^{20} 0.9725; n_D^{20} 1.4565; found MR 76.65; calculated for $C_{13}H_{28}O_3PN$ MR 75.05.

Found %: P 11.02; 10.95

$C_{13}H_{28}O_3PN$. Calculated %: P 11.18

Synthesis of n-heptyl ester of ethyldiethylamidoformylphosphonic acid. Reactants were 1 g sodium (with excess), 5.5 g n-heptyl ester of ethylphosphonous acid and 3.9 g diethylcarbomyl chloride. The heptyl ester of ethyldiethylamido formylphosphonic acid was obtained in amount of 2.5 g or 30% of the theoretical: b.p. 143-145° (2 mm); d_4^{20} 0.9817; n_D^{20} 1.4565; found MR 80.75; calculated for $C_{14}H_{30}O_3PN$ MR 79.67.

Found %: P 10.67; 10.69

$C_{14}H_{30}O_3PN$. Calculated %: P 10.65

Synthesis of n-octyl ester of ethyldiethylamidoformylphosphonic acid. Materials used were 1 g sodium (with excess), 5.3 g n-octyl ester of ethylphosphonous acid and 3.5 g diethylcarbamyl chloride. The n-octyl ester of ethyldiethylamidoformylphosphonic acid had the following constants: b.p. 137-138°(0.5 mm) d_4^{20} 0.9782, n_D^{20} 1.4618; found MR 85.80; calculated for $C_{15}H_{32}O_3PN$ MR 84.29; yield of ester 3.5 g, or 42% of theoretical.

Found %: P 10.36; 10.28

$C_{15}H_{32}O_3PN$. Calculated %: P 10.18

Synthesis of n-nonyl ester of ethyldiethylamidoformylphosphonic acid. The synthesis was performed with 1.5 g sodium (with excess), 7.2 g n-nonyl ester of ethylphosphonous acid and 4.5 g diethylcarbamyl chloride. Fractional distillation of the reaction products in vacuum from an Arbuzov flask gave the n-nonyl ester with the following constants: b.p. 145-147° (1.5 mm); d_4^{20} 0.9702; n_D^{20} 1.4612; found MR 90.38, calculated for $C_{16}H_{33}O_3PN$ MR 88.91; yield 5.8 g or 55% of theory.

Found %: P 9.65; 9.61

$C_{16}H_{32}O_3PN$ Calculated %: P 9.73

Synthesis of n-decyl ester of ethyldiethylamidoformylphosphonic acid. Synthesis was performed with 1 g sodium (with excess), 6 g decyl ester of ethylphosphonous acid and 3.5 g diethylcarbamyl chloride. Vacuum fractionation from an Arbuzov flask gave the n-decyl ester of ethyldiethylamidoformylphosphonic acid with the following constants: 160-162° (1.5 mm); d_4^{20} 0.9630; n_D^{20} 1.4600; found MR 94.84; calculated for $C_{17}H_{34}O_3PN$ MR 93.52; yield 4.6 g, or 53.5% of theory.

	Found %:	P 9.32; 9.28
$C_{17}H_{34}O_3PN$.	Calculated %:	P 9.3

SUMMARY

Reaction of diethylcarbamyl chloride with the sodium salts of the partial esters of ethylphosphonous acid gave esters of ethyldiethylamidoformylphosphonic acid.

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Received June 19, 1953

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NEW METHOD OF SYNTHESIS OF ESTERS OF PHOSPHONIC AND THIOPHOSPHONIC ACIDS

16. SYNTHESIS OF ESTERS OF MONO-, DIPHOSPHONO-, AND THIO- PHOSPHONOCARBOXYLIC ACIDS

A. N. Pudovik and D. Kh. Yarmukhametova

As one of us has shown, in the presence of alcoholates of alkali metals the dialkylphosphorous acids very easily add on to esters of unsaturated mono- and dibasic acids and ketocarboxylic acids [1], unsaturated nitriles [2], aldehydes [3] and ketones [4], vinyl acetate [5] and imines [6] with formation, respectively, of esters of phosphonocarboxylic acids their nitriles and amines, esters of ketophosphonic and unsaturated hydroxyphosphonic esters, esters of phosphoethyl acetate, substituted aminophosphonic esters, etc. Esters of unsaturated carboxylic acids used in reactions with dialkylphosphorous acids were esters of acrylic, methacrylic, crotonic, cinnamic, maleic and acetylenedicarboxylic acids. In the majority of cases the esters of phosphonocarboxylic acids were obtained in high yields.

Recently Kabachnik and Mastryukova described the synthesis of dialkylthiophosphorous acids [7]. Dialkylthiophosphorous acids were also prepared in our laboratory in 1950-1951 by Nikonorov and one of us and used for the synthesis of esters of ketothiophosphonic and unsaturated hydroxythiophosphonic acids [8]. In continuation of these investigations, it appeared to us of interest to undertake the addition of dialkylthiophosphorous acids to esters of unsaturated carboxylic acids, to synthesize previously unknown esters of thiophosphonocarboxylic acids and to study their properties. The addition was performed in presence of sodium alkoxides. The course of the reactions may be represented by the following scheme:

$$(RO)_2PSH + RONa \rightleftharpoons (RO)_2PSNa + ROH$$

$$R'\overset{\delta+}{C}H=\overset{\delta+}{C}R''-COOR''' + (RO)_2PSNa^{+} \rightarrow R'CH(P(S)(OR)_2)-CR''NaCOOR'''$$

or

$$R'-CH(P(S)(OR)_2)-CR''=C(ONa)(OR''') \xrightarrow{(RO)_2PSH} R'-CH(P(S)(OR)_2)-CHR''-COOR''' + (RO)_2P(S)Na \text{ etc.}$$

where $R = C_2H_5$, n- C_3H_7, n- C_4H_9, i- C_4H_9; $R' = H, CH_3, C_6H_5, COOR'''$;

$R'' = H, CH_3$; $R''' = CH_3, C_2H_5$, n- C_3H_7; iso-C_4H_9, n- C_4H_9.

It should be noted that when carrying out the addition of dialkylthiophosphorous acids to esters of unsaturated acids containing different radicals in the carboxyl groups, it was not possible in all cases, due to transesterification, to obtain completely pure products. Esters of thiophosphonocarboxylic acids were synthesized in the pure form when using dialkylthiophosphorous acids, esters of carboxylic acids and alkoxides of alcohols with identical radicals in the alkoxyl and carboxyl groups. The constants and yields of the resultant esters of dialkylthiophosphonocarboxylic acids are set forth in Table 1.

We see that the esters of thiophosphonopropionic, thiophosphonoisobutyric, thiophosphonophenylpropionic, thiophosphonosuccinic acids were obtained in quite high yields.

Hydrolysis of the methyl ester of β-(diethylthiophosphono)-propionic acid gave an acid with m.p. 162-162.5°. A strong odor of hydrogen sulfide was noticed when the tube was opened and the solution evaporated. Analysis of

this acid showed it to be free from sulfur. Analysis for phosphorus gave results very close to the theoretical requirement for β-phosphonopropionic acid. A. E. Arbuzov gave m.p. 166-166.5° for β-phosphonopropionic acid. A mixed sample of the acid obtained by hydrolysis of the ester of β-(diethylthiophosphono) propionic acid with the β-phosphonothiopropionic acid synthesized by hydrolysis of the ester of β-(di ethylphosphono)-propionic acid melted at 162-163°.

TABLE 1

No.	Formula	B.p. in °C (pressure in mm Hg)	d_4^{20}	n_D^{20}	Yield in %
1	$(C_2H_5O)_2\overset{\overset{S}{\|}}{P}-CH_2CH_2COOCH_3$	110 (1.5)	1.1225	1.4652	86
2	$(C_2H_5O)_2P-\overset{S}{\overset{\|}{C}}H-\overset{CH_3}{\overset{\|}{C}}H-COOCH_3$	98-98.5 (0.5)	1.0975	1.4646	88
3	$(C_3H_7O)_2\overset{\overset{S}{\|}}{P}-CH_2-\overset{CH_3}{\overset{\|}{C}}H-COOC_3H_7$	136-136.5 (1)	1.0340	1.4630	83
4	$(C_4H_9O)_2\overset{\overset{S}{\|}}{P}-CH_2-\overset{CH_3}{\overset{\|}{C}}H-COOC_4H_9\text{-p}$	159 (0.5)	1.0061	1.4600	81
5	$(i-C_4H_9O)_2\overset{\overset{S}{\|}}{P}-CH_2-\overset{CH_3}{\overset{\|}{C}}H-COOC_4H_9\text{-i}$	145 (1)	1.0000	1.4600	70
6	$(C_2H_5O)_2\overset{\overset{SCH_3}{\|}}{P}-CH-CH_2COOC_2H_5$	108-109 (1)	1.0777	1.4612	80
7	$(C_2H_5O)_2\overset{\overset{S}{\|}}{P}-\underset{\underset{C_6H_5}{\|}}{C}H-CH_2-COOC_2H_5$	158.5 (1)	1.1278	1.5112	76
8	$(C_2H_5O)_2\overset{\overset{S}{\|}}{P}-\underset{\underset{COOC_2H_5}{\|}}{C}H-CH_2-COOC_2H_5$	146.5 (1)	1.1319	1.4630	78

Consequently the process of hydrolysis of the ester of β-(diethylthiophosphono) propionic acid proceeds with cleavage of sulfur from the thiophospho group and its substitution by oxygen

$$(RO)_2\overset{\overset{S}{\|}}{P}-CH_2CH_2COOR \xrightarrow[H_2O]{2HCl} (HO)_2\overset{\overset{O}{\|}}{P}-CH_2CH_2COOH + 2RCl + ROH + H_2S.$$

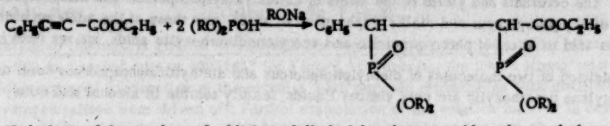
In order to obtain confirmation that the cleavage of sulfur from the thiophosphono group, proceeding during hydrolysis of the ester of β-(diethylthiophosphono)-propionic acid is not fortuitous, the ethyl ester of ethylthiophosphonic acid was synthesized and then hydrolyzed. In this case also, although less easily and less completely, cleavage of sulfur was effected.

In one of our previous investigations it was shown [1] that acid esters of ethyl- and phenylphosphonous acid readily add on to esters of acrylic and methacrylic acids with formation of esters of the corresponding carboxyalkylphosphonic acids. In a similar manner we synthesized the products of addition of the above acids to the esters of crotonic, cinnamic and maleic acids. The constants and yields of the synthesized esters of carboxyethylphosphonic acids are set forth in Table 2.

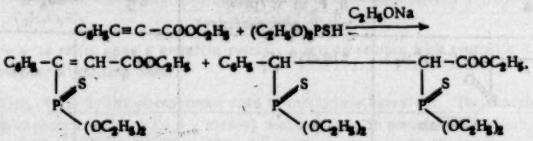
Hydrolysis of these esters gave: α-methyl-β-carboxydiethylphosphonic acid with m.p. 82-82.5°; α-phenyl-β-carboxydiethylphosphonic acid with m.p. 138-138.5°; and α,β-dicarboxydiethylphosphonic acid with m.p. 131-131.5°

Interesting results were obtained by addition of esters of phosphorus acids to esters of phenylpropiolic acid. Addition of dimethylphosphorous and diethylphosphorous acids to the methyl and ethyl esters of phenylpropiolic acid, both when using equimolar ratios of reactants and when using an excess of the dialkylphosphorous acids, gives in the pure form only esters of diphosphonophenylpropionic acid. The structure of the addition products has not been

rigorously established, but it is most probable that their phosphono groups are located at both of the carbon atoms:



Hydrolysis of the product of addition of diethylphosphorous acid to the methyl ester of phenylpropiolic acid gave diphosphonophenylpropionic acid with m.p. 113-115°. Addition of diethylthiophosphorous acid to the ethyl ester of phenylpropiolic acid yielded products of addition of both one and two molecules of acid:



On addition of the ethyl ester of ethylphosphonous acid to the ethyl ester of phenylpropiolic acid, we succeeded in isolating only the product of addition of one molecule of the acid ester. Diethylthiophosphorous acid adds on with great facility to the diethyl ester of acetylenedicarboxylic acid, the main product of reaction being that of the addition of two molecules of acid:

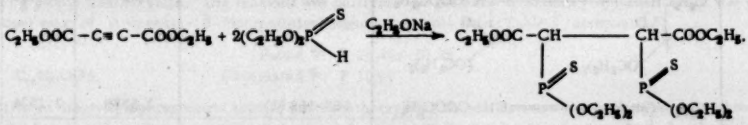
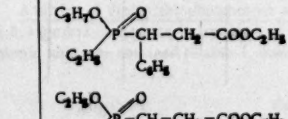
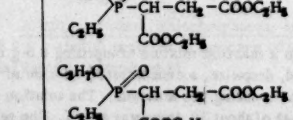
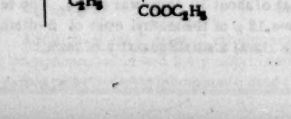


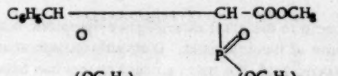
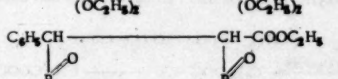
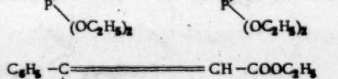
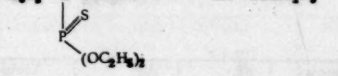
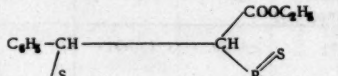
TABLE 2

No.	Formula	B.p. in °C (pressure in mm mercury)	n_D^{20}	d_4^{20}	Yield in %
1		118-120 (1.5)	1.4492	1.0564	78
2		154-155 (1.5)	1.5025	1.1128	77
3		157-158 (0.5)	1.5040	1.1048	76
4		164-166 (1)	1.5012	1.0844	69
5		142 (1)	1.4481	1.1142	60
6		151-152.5 (0.5)	1.4510	1.1015	57

In spite of repeated fractionation it was not possible to isolate products of addition of one molecule from the lower boiling fractions. The constants and yields of the esters of carboxyalkylphosphonic and thiophosphonic acids obtained by addition of dialkylphosphorous and dialkylthiophosphorous acids, also those of the addition of the ethyl ester of ethylphosphonous acid to esters of phenylpropiolic and acetylenedicarboxylic acids, are set forth in Table 3.

The products of addition of two molecules of diethylphosphorous and diethylthiophosphorous acids to esters of phenylpropiolic and acetylene dicarboxylic are very viscous liquids, readily soluble in alcohol and ether, insoluble in water.

TABLE 3

No.	Formula	B. P. in °C (pressure in mm mercury)	n_D^{20}	d_4^{20}	Yield in %
1		210-212 (4)	1,5072	–	46
2		208 (2)	1,4939	1,2086	50
3		202 (0,5)	1,4915	1,1754	47
4		168-169 (1)	1,5369	1,1534	32
5		212 (1)	1,5271	–	15
6		147-148 (0,5)	1,5082	1,1054	30
7		185 (1)	1,4885	1,1890	21

EXPERIMENTAL

Addition of diethylthiophosphorous acid to methyl acrylate. To a reaction mixture comprising 8,5 g of diethylthiophosphorous acid and 4,8 g of methyl acrylate was slowly added, dropwise, a concentrated solution of sodium ethylate in absolute ethyl alcohol. Considerable heat was developed during the reaction. The solution of sodium ethylate was added until the mixture ceased to evolve heat; a total of about 10 drops was added. The reaction mixture was heated on the water bath for 2 hours. Fractionation gave 12 g of the methyl ester of β-diethylthiophosphonopropionic acid (Table 1, compound 1) and (at the bottom of the flask) a small quantity of resin.

Found %: P 13.17; 13.24

$C_9H_{17}O_4PS$. Calculated %: P 12.92

Hydrolysis of the methyl ester of β-diethylthiophosphonopropionic acid. 4.3 g ester was heated with 45 ml dilute (1:1) HCl in a sealed tube at 130-140° for 8 hours. On opening the tube a strong odor of hydrogen sulfide was noticed. After repeated evaporation of the mixture with periodic replenishing with distilled water the hydrochloric acid and hydrogen sulfide were driven off. Further evaporation of the solution resulted in deposition of crystals which after three recrystallizations from water and drying in the air melted at 162-162.5°.

Found %: P 20.24; 20.20

$C_3H_7O_4SP$. Calculated %: P 18.23

$C_3H_7O_4P$. Calculated %: P 20.13

Analysis for sulfur gave a negative result. A mixed sample with synthetic β-phosphonopropionic acid did not give a depression of melting point.

Addition of diethylthiophosphorous acid to methylmethacrylate. The reaction was carried out with 6.6 g diethylthiophosphorous acid and 4.3 g methyl methacrylate in presence of sodium ethylate. There was obtained 9.6 g methyl ester of α-methyl-β-diethylthiophosphonopropionic acid (Table 1, compound 2).

Found %: P 12.51

$C_9H_{19}O_4PS$. Calculated %: P 12.21

Addition of dipropylthiophosphorous acid to propyl methacrylate. Reactants were 5.3 g dipropylthiophosphorous acid and 3.7 g propyl methacrylate. The reaction was performed in presence of sodium propylate. There was obtained 6.8 g propyl ester of α-methyl-β-dipropylthiophosphonopropionic acid (Table 1, compound 3).

Found %: P 10.19; 10.29

$C_{13}H_{27}O_4PS$. Calculated %: P 10.00

Addition of dibutylthiophosphorous acid to butyl methacrylate. Reactants were 4.1 g dibutylthiophosphorous acid and 2.8 g butyl methacrylate in presence of sodium butylate. 5.6 g butyl ester of α-methyl-β-dibutylthiophosphonopropionic acid was obtained (Table 1, compound 4).

Found %: P 9.17; 9.23

$C_{16}H_{33}O_4PS$. Calculated %: P 8.81

Addition of diisobutylthiophosphorous acid to isobutyl methacrylate. Reaction was effected between 3.5 g diisobutylthiophosphorous acid and 2.4 g isobutyl methacrylate in presence of sodium isobutylate. 4.2 g isobutyl ester of α-methyl-β-diisobutylthiophosphonopropionic acid was obtained (Table 1, compound 5).

Found %: P 9.22; 9.11

$C_{16}H_{33}O_4PS$. Calculated %: P 8.81

Addition of diethylthiophosphorous acid to ethyl crotonate. Reactants were 4.6 g diethylthiophosphorous acid and 3.4 g ethyl crotonate. Yield 6.1 g of the ethyl ester of β-methyl-β-diethylthiophosphonopropionic acid (Table 1, compound 6).

Found %: P 11.68; 11.64

$C_{10}H_{21}O_4PS$. Calculated %: P 11.57

Addition of diethylthiophosphorous acid to ethyl cinnamate. 3 g diethylthiophosphorous acid was reacted with 3.3 g ethyl cinnamate in presence of sodium ethylate. 5.2 g ethyl ester of β-phenyl-β-diethylthiophosphonopropionic acid was obtained (Table 1, compound 7).

Found %: P 9.57; 9.70

$C_{15}H_{23}O_4PS$. Calculated %: P 9.39

Addition of diethylthiophosphorous acid to diethyl maleate. 2.5 g diethylthiophosphorous acid was reacted with 2.8 g diethyl maleate in presence of sodium ethylate to give 4.1 g diethyl ester of diethylthiophosphonosuccinic acid (Table 1, compound 8).

Found %: P 9.75; 9.68

$C_{12}H_{23}O_6PS$. Calculated %: P 9.51

Addition of ethyl ester of ethylphosphonous acid to ethyl crotonate. Reaction between 2.6 g ethyl ester of ethylphosphonous acid and 2.4 g ethyl crotonate in presence of sodium ethoxide gave 3.7 g ethyl ester of α-methyl-β-(carboxyethyl)-diethylphosphonic acid (Table 2, compound 1).

Found %: P 13,22; 13,40

$C_{10}H_{21}O_4P$. Calculated %: P 13,14

Addition of ethyl ester of phenylphosphonous acid to ethyl crotonate. Reaction between 3,9 g ethyl ester of phenylphosphonous acid and 2,6 g ethyl crotonate in presence of sodium ethylate gave 5 g ethyl ester of α-methyl- β-(carboxyethyl)-ethyl-phenylphosphonic acid (Table 2, compound 2).

Found %: P 10,91

$C_{14}H_{21}O_4P$. Calculated %: P 10,91

Hydrolysis of ethyl ester of α-methyl- β-(carboxyethyl)-ethylphosphonic acid. 4,1 g ester was heated with 4 ml dilute HCl (1:1) in a sealed tube at 140° for 8 hours. After repeated evaporation with periodic addition of water to the reaction mixture and final evaporation, 2,3 g crystals came down. After three recrystallizations from water, pure α-methyl-β-carboxydiethylphosphonic acid was obtained with m.p. 82-82,5°. Yield 1,5 g or 70 % of the theoretical.

Found %: P 13,33

$C_8H_{17}O_4P$. Calculated %: P 13,59

Addition of ethyl ester of ethylphosphonous acid to ethyl cinnamate. Reaction of 3,9 g ethyl ester of ethylphosphonous acid with 5,7 g ethyl cinnamate gave 7,3 g ethyl ester of α-phenyl- β-(carboxyethyl)-diethylphosphonic acid (Table 2, compound 3).

Found %: P 10,49

$C_{16}H_{25}O_4P$. Calculated %: P 10,40

Hydrolysis of ethyl ester of α-phenyl- β-(carboxyethyl)-diethylphosphonic acid. 4,9 g ester was heated with 40 ml dilute HCl (1:1) in a sealed tube at 140° for 8 hours. After repeated evaporation with periodic addition of water to the reaction mixture followed by a final evaporation, 3,2 g crystals came down. After two recrystallizations from water, they melted at 138-138,5°. Yield 82% of theoretical.

Found %: P 12,66

$C_{11}H_{17}O_4P$. Calculated %: P 12,80

Addition of n-propyl ester of ethylphosphonous acid to ethyl cinnamate. Reaction between 2,4 g n-propyl ester of ethylphosphonous acid and 3,1 g ethyl cinnamate in presence of sodium propylate gave 3,8 g n-propyl ester of α-phenyl-β-(carboxyethyl)-diethylphosphonic acid (Table 2, compound 4).

Found %: P 9,79; 9,88

$C_{16}H_{25}O_4P$. Calculated %: P 9,93

Addition of ethyl ester of ethylphosphonous acid to diethyl maleate. Reaction between 2,1 g ethyl ester of ethylphosphonous acid and 3 g diethyl maleate gave 3 g ethyl ester of α, β-di(carboxyethyl)-diethylphosphonic acid (Table 2, compound 5).

Found %: P 10,46; 10,54

$C_{12}H_{23}O_6P$. Calculated %: P 10,56

Addition of n-propyl ester of ethylphosphonous acid to diethyl maleate. Reaction between 2,5 g n-propyl ester of ethylphosphonous acid and 3,15 g diethyl maleate in presence of sodium ethylate gave 3,2 g n-propyl ester of α,β-di(carboxyethyl)-diethylphosphonic acid (Table 2, compound 6).

Found %: P 9,90; 9,93

$C_{13}H_{25}O_6P$. Calculated %: P 10,06

Hydrolysis of n-propyl ester of α,β-di(carboxyethyl)-diethylphosphonic acid. 6 g ester was heated with 40 ml dilute HCl (1:1) in a sealed tube at 140° for 8 hours. After repeated evaporation of the reaction mixture with periodic addition of distilled water, final evaporation gave 3 g crystals. These could not be recrystallized from water or other solvents. The crystals were thoroughly washed with methyl-ethyl ketone. M.p. of crystals 131-131,5°. Yield of acid 75 % of theoretical.

Found %: P 14,67

$C_6H_{11}O_6P$. Calculated %: P 14,76

Addition of dimethylphosphorous acid to methyl phenylpropiolate. Reaction between 6,2 g dimethylphosphorous acid and 10 g methyl phenylpropiolate in presence of sodium ethoxide gave 7,3 g methyl ester of α, β-di-(dimethylphosphono)-phenylpropionic acid (Table 3, compound 1). The compound crystallized on standing. After recrystallization from benzene the crystals melted at 109-111°.

Found %: P 16.24; 16.37

$C_{14}H_{22}O_5P_2$. Calculated %: P 16.32

Addition of diethylphosphorous acid to methyl phenylpropiolate. Reaction between 14.6 g diethylphosphorous acid and 7.5 g methyl phenylpropiolate in presence of sodium ethylate gave 12.5 g methyl ester of α,β-di-(diethylphosphono)-phenylpropionic acid (Table 3, compound 2).

Found %: P 14.02; 13.98

$C_{18}H_{30}O_9P_2$. Calculated %: P 14.24

Hydrolysis of methyl ester of α, β-di-(diethylphosphono)-phenylpropionic acid. 4.5 g ester was heated in a tube with dilute HCl (1:1) for 6 hours at 130°. After repeated evaporation with fresh quantities of water, final evaporation gave crystals with m. p. 113 -115°.

Found %: P 19.8; 19.95

$C_9H_{13}O_5P_2$. Calculated %: P 20.00

Addition of diethylphosphorous acid to ethyl phenylpropiolate. Reaction between 10 g diethylphosphorous acid and 5.5 g ethyl phenylpropiolate gave 7 g ethyl ester of α, β-di-(diethylphosphono)-phenylpropionic acid (Table 3, compound 3).

Found %: P 13.96; 13.88

$C_{19}H_{32}O_9P_2$ Calculated %: P 13.78

Addition of diethylthiophosphorous acid to ethyl phenylpropiolate. Reaction between 10.8 g diethlthiophosphonous acid and 6.1 g ethyl phenylpropiolate was performed in presence of sodium ethylate. Fractionation of the reaction mixture gave 2.5 g ethyl ester of -(diethylthiophosphono)-cinnamic acid (Table 3, compound 4) and 2.4 g ethyl ester of α, β-di-(diethylthiophosphono)-phenylpropionic acid (Table 3, compound 5). The latter is a very viscous liquid.

Analysis of compound 4

Found %: P 9.75; 9.68

$C_{18}H_{21}O_4PS$. Calculated %: P 9.45

Analysis of compound 5

Found %: P 12.66; 12.87

$C_{19}H_{32}O_9P_2S_2$. Calculated %: P 12.86

Addition of ethyl ester of ethylphosphorous acid to ethyl phenylpropiolate. Reaction of 4.2 g ethyl ester of ethylphosphorous acid with 3 g ethyl phenylpropiolate gave 1.5 g addition product (Table 3, compound 6).

Found %: P 10.57

$C_{19}H_{32}O_9P_2$. Calculated %: P 10.45

Addition of diethylthiophosphorous acid to diethyl acetylenedicarboxylate. Reaction was effected between 7.2 g diethylthiophosphorous acid and 4 g diethyl acetylenedicarboxylate. There was obtained 2.3 g diethyl ester of α,β-di-(diethylthiophosphono)-succinic acid (Table 3, compound 7).

Found %: P 13.25; 13.00

$C_{18}H_{32}O_9P_2S_2$. Calculated %: P 12.97

SUMMARY

1. Addition of diethylthiophosphorous acid to esters of acrylic, methacrylic, cinnamic and maleic acids gave high yields of esters of dialkylthiophosphonopropionic, dialkylthiophosphonoisobutyric, dialkylthiophosphonophenylpropionic and dialkylthiophosphonosuccinic acids.

2. Addition was effected of esters of ethyl- and phenylphosphorous acids to esters of crotonic, cinnamic and maleic acids.

3. Addition of dialkylphosphorous acids, of ethylethylphosphonite and of ethyl diethlthiophosphorite to esters of phenylpropiolic and acetylenedicarboxylic acids gave esters of dialkylphosphono- and dialkylthiophosphono- cinnamic acid, esters of di-(dialkylphosphono)- and di-(diethylthiophosphono)- phenylpropionic acid and esters of di-(diethylthiophosphono)-succinic acid.

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Received April 1, 1953

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1 See Consultants Bureau Translation, p. p. 537, 1189, 2103.
2 " " " p. 2035.
3 " " " p. 821.
4 " " " p. p. 657; 803.
5 " " " p. 531.
6 " " " p. 825.
7 " " " p. 1415.
8 " " " p. 537.
9 " " " p. 831;
10 " " " p. 661.
11 " " " p. 825.

MECHANISM OF REACTION OF PHOSPHORUS PENTACHLORIDE WITH CARBOXYLIC ACID AMIDES*

A. V. Kirsanov

In all textbooks, handbooks, and reference books of organic chemistry, it is stated that the action of phosphorus pentachloride on unsubstituted amides of carboxylic acids leads to formation of phosphorus oxychloride and amidochlorides:

$$RCONH_2 + PCl_5 \longrightarrow POCl_3 + RCCl_2NH_2.$$

It is impossible, however, to isolate the amidochlorides in the pure form since they are extremely unstable and break down in the conditions of formation

$$RCCl_2NH_2 \longrightarrow HCl + RCCl{=}NH,$$

i.e., formation takes place of hydrogen chloride and imidochlorides which likewise decompose and the final products are the nitriles of the carboxylic acids:

$$RCCl{=}NH \longrightarrow HCl + RC{\equiv}N.$$

Such a mechanism of the reaction between phosphorus pentachloride and carboxylic acid amides was proposed as far back as 1858 by Gerhardt [1]; in 1877 it was studied by Wallach [2] and since then it has been unreservedly accepted by all scientists who have investigated the reaction of phosphorus pentachloride with carboxylic acid amides [3].

Wallach encountered several reactions which could not be explained by his scheme and called for additional clarifications; of these the most important are the following: on reacting phosphorus pentachloride with trichloroacetamide, Wallach [2] obtained not the amido chloride but a phosphorus-containing compound whose composition and molecular weight corresponded to the formula C_2Cl_6ONP, and he attributed to it the structure $CCl_3CCl{=}NPOCl_2$. In order to account for the formation of this substance, Wallach proposed a supplementary scheme according to which the imidochloride formed in this reaction can enter into reaction with phosphorus oxychloride:

$$RCCl{=}NH + POCl_3 \longrightarrow HCl + RCCl{=}NPOCl_2 .$$

i.e. with formation of chlorides of imidochloride-N-phosphoric acids. Compounds of a similar type were later prepared by Steinkopf [4] who accepted for them the mechanism of formation and the structure proposed by Wallach.

It must be noted that when discussing the possible structure of the phosphorus-containing compound obtained from trichloroacetamide and phosphorus pentachloride, Wallach considered only two formulas, namely $CCl_3CONClPCl_2$ and $CCl_3CCl{=}NPOCl_2$ and overlooked a third theoretically possible formula $CCl_3CON{=}PCl_3$. It should also be pointed out that the supplementary hypothesis of reaction of the imidochlorides with phosphorus oxychloride was not checked experimentally, has never been confirmed, and obviously originated in the desire to give some sort of explanation of the mechanism of the reaction through intermediate formation of amidochlorides or imidochlorides.

A second fact which did not fit in with Wallach's scheme was the reaction (which he discovered) of the amidochloride prepared from ethyl oxamate with phenols and alcohols [5]. In this reaction in place of the expected iminoesters which should have been formed according to the scheme:

$$C_2H_5COCCl_2NH_2 + HOR \longrightarrow C_2H_5OCO\overset{\overset{OR}{|}}{C}{=}NHHCl + HCl,$$

there were actually obtained ethyl chloride and esters of oxamic acid with the same alcohol which was introduced into the reaction, i.e. the process took place according to the scheme:

* Report to the Session of the Division of Chemical Sciences of the Academy of Sciences of the USSR, April 23, 1954.

$$C_6H_5OCOCl_2NH_2 + HOR \rightarrow C_6H_5Cl + HCl + ROCOCONH_2.$$

Wallach did not give any convincing explanation of this mechanism.

In 1909 Titherley and Worrall [6] studied the action of phosphorus pentachloride on benzamide and established that the first product of the reaction is evidently a substance with the composition $C_6H_5CONPCl_3$, but they failed to isolate this compound in the pure state. On exposing a solution of the original product to the action of atmospheric moisture, Titherley and Worrall obtained a nearly quantitative yield of benzoylaminophosphoryl chloride $C_6H_5CONHPOCl_2$ which on heating broke down quantitatively to benzonitrile, hydrogen chloride, phosphorus oxychloride and metaphosphoric acid.

Notwithstanding all these inconsistencies, Wallach's scheme has not been subjected to criticism since its publication in 1877 to the present day and is cited as incontestable fact not only in reference books but even in all elementary textbooks of organic chemistry.

Recently it was found that amides of sulfonic acids easily and quantitatively react with phosphorus pentachloride with evolution of hydrogen chloride and formation of the corresponding trichlorophosphazosulfo compounds according to the scheme:

$$RSO_2NH_2 + PCl_5 \rightarrow 2HCl + RSO_2N{=}PCl_3.$$

The reaction is general in character and proceeds with equal ease for sulfamic acid [7], sulfamide [8], amides of aromatic sulfonic acids [9] and amides of alicyclic sulfonic acids.

The mechanism of reaction of phosphorus pentachloride with amides of sulfuric acid is probably as follows. At the outset the PCl_4^+ ion attaches itself to the coordinatively unsaturated nitrogen atom

$$RSO_2NH_2 + PCl_4^+ \rightarrow RSO_2\underset{\displaystyle PCl_4}{\overset{|}{N}}H_2^+$$

Then the unstable intermediate product is stabilized with splitting-off of hydrogen chloride and a proton:

$$RSO_2\underset{\displaystyle PCl_4}{\overset{|}{N}}H_2^+ \rightarrow HCl + RSO_2N{=}PCl_3 + H^+.$$

The proton reacts with the PCl_6^- ion with formation of hydrogen chloride and PCl_5 which immediately breaks down to ions of PCl_4^+ and PCl_6^-.

Carboxylic acid amides are not strictly analogs of amides of sulfonic acids, but the nitrogen atom of the amides is likewise coordinatively unsaturated and is likewise linked to two atoms of hydrogen, as is the nitrogen atom of sulfonic acid amides. There is therefore good reason to assume that the reaction of phosphorus pentachloride with carboxylic acid amides must proceed according to the same mechanism as for sulfonic acid amides, i.e. with formation of trichlorophosphazoacyls according to the scheme:

$$RCONH_2 + PCl_4^+ \rightarrow RCO\underset{\displaystyle PCl_4}{\overset{|}{N}}H_2^+ \rightarrow H^+ + HCl + RCO{=}NPCl_3.$$

It would undoubtedly be wrong, however, to suggest that the properties of trichlorophosphazosulfonacyls must be similar to the properties of trichlorophosphazosulfo compounds. First, these two classes of compounds must differ in thermal stability. On cleavage, the trichlorophosphazoacyls must form phosphorus oxychloride and stable, thermodynamically "advantageous" nitriles:

$$RCON{=}PCl_3 \rightarrow POCl_3 + RCN.$$

Hence, the thermal cleavage of trichlorophosphazoacyls must proceed with great facility and with good yields.

Thermal cleavage of trichlorophosphazosulfo compounds must yield phosphorus oxychloride and unstable alkyl or aryl sulfans which are evidently thermodynamically not too "advantageous" and which have been hitherto unknown:

$$RSO_2N{=}PCl_3 \rightarrow POCl_3 + RSON.$$

Consequently the thermal cleavage of trichlorophosphazosulfo compounds must proceed with great difficulty and with poor yields, as is confirmed by experimental results [10].

We thus have sufficient and reliable experimental and theoretical evidence to throw doubt upon the correctness of Wallach's mechanism, and we may suggest that the action of phosphorus pentachloride on carboxylic acid amides actually leads not to amidochlorides but to trichlorophosphazoacyls which easily break down to phosphorus oxychloride and nitriles:

$$RCONH_2 + PCl_5 \rightarrow 2HCl + RCON{=}PCl_3 + POCl_3 + RCN$$

Formation of imidochlorides is readily accounted for by the following reaction of HCl with nitriles: RCN + $\rightarrow$RCCl=NH or more probably: $RC{\equiv}NH^+ + Cl^-$. The latter reaction does not call for confirmation since it is the usual method of preparation of imidochlorides [11]. The newly proposed mechanism does not, however, explain the formation of amidochlorides which, according to the generally accepted scheme of Wallach, are the first products of the reaction. A detailed study of Wallach's original papers established that Wallach did not isolate in the pure state a single one of the amidochlorides of the type of $RCCl_2NH_2$ in the reaction of phosphorus pentachloride with carboxylic acid amides. The crude products obtained by Wallach were only analyzed for chlorine, in which connection the analytical data were very different from the calculated theoretical values and frequently were more consistent with the composition of trichlorophosphazoacyls than with the composition of amidochlorides.

In a study of the reaction of acetamide and benzamide with phosphorus pentachloride, Wallach failed to isolate any pure substances, for which reason he wrote: "acetamide is not a suitable model for the study of the reaction of phosphorus pentachloride with carboxylic acid amides". He chose as a model the ethyl ester of oxamic acid. This choice must be considered most unfortunate, for oxalic acid and its amides differ sharply in properties both from the common monobasic carboxylic acids and from all other dibasic carboxylic acids and their amides. It suffices to recall the exceptionally easy oxidizability of oxalic acid and its derivatives, sharply differentiating it from the overwhelming majority of the remaining saturated carboxylic acids, or the characteristic reaction of oxalic acid esters with phosphorus pentachloride. Moreover, we must reckon with the possibility of reaction of phosphorous pentachloride not only with the carbamido group but also with the carbethoxy. Consequently the data obtained for ethyl oxamate cannot be regarded as typical of the behavior of amides of all other carboxylic acids. Moreover, even these data, when examined critically, do not provide any evidence that the first product of reaction of ethyl oxamate with phosphorus pentachloride is the corresponding amidochloride. Wallach reported that one molecule of phosphorus pentachloride acts on ethyl oxamate without evolution of hydrogen chloride, the product being a colorless, transparent liquid which deposits crystals on cooling, but Wallach did not succeed in isolating the crystals in the pure state. In the best case the chlorine content of this substance was 4.12% less than required for the amidochloride. Other analyses were not performed. No characteristic reactions demonstrating that the substance really was an amidochloride were carried out, if we except the thermal cleavage of the crude reaction product which led to a low yield of cyanoformic ester.

Wallach also gives a detailed description of the formation from the reaction mixture by the action of atmospheric moisture of a pure compound with the composition $C_4H_6O_3Cl_4NP$, discusses the possible structure of the substance and expresses surprise apropos of the fact that the substance is undoubtedly only formed in presence of atmospheric moisture. It is impossible to reconcile the formation of this substance with Wallach's hypothesis of primary formation of an amidochloride with the structure $C_2H_5OCOCCl_2NH_2$, since it is altogether improbable that under the action of atmospheric moisture phosphorus oxychloride could add on to an amidochloride, while in the absence of atmospheric moisture the substance is not formed. Wallach did not put forward any explanation of the formation of the compound $C_4H_6O_3Cl_4NP$ but nevertheless considered that the formation of amidochlorides by the action of phosphorus pentachloride on carboxylic acid amides had been completely demonstrated. Thus a close examination of Wallach's paper shows that the formation of an amidochloride during the action of phosphorus pentachloride on ethyl oxamate was not only not proved but was even extremely improbable.

The reaction of phosphorus pentachloride with carboxylic acid amides was studied not only by Wallach but also by a number of other workers [3, 4, 6]. None of them succeeded in isolating amidochlorides and none of them demonstrated their formation by the action of phosphorus pentachloride on unsubstituted carboxylic acid amides by any trustworthy indirect methods. Consequently there are no reliable experimental data to prove that amidochlorides are obtained by the action of phosphorus pentachloride on carboxylic acid amides. It was only due to the great reputation of Wallach as a scientist that his unfounded and erroneous conclusions about the reaction of phosphorus pentachloride with carboxylic acid amides were accepted quite uncritically and have been regarded as entirely true for over 75 years.

For a final solution of the problem it was necessary to make an experimental study of the reaction of phosphorus pentachloride with carboxylic acid amides and to check and clarify the conflicting and confused results of Wallach regarding the reaction of phosphorus pentachloride with ethyl oxamate.

The first substance selected as a model was benzamide, since the data obtained with benzamide can be applied with minor reservations to amides of other carboxylic acids. It was found that phosphorus pentachloride readily reacts with benzamide. On conducting the reaction between equivalent amounts of reactants in carbon tetrachloride solution at 70°, the process is completed in the course of a few minutes and about 90% of the hydrogen chloride is evolved according to the equation:

$$C_6H_5CONH_2 + PCl_5 \rightarrow 2HCl + C_6H_5CON{=}PCl_3$$

After the solvent had been driven off in vacuum at 70°, there remained a colorless transparent liquid which rapidly crystallized completely. The amount of crude product corresponded to 97.7% of that according to the above equation. The melting point of the crude product was 58° (thermometer bulb in the liquid, disappearance of the last crystal). The substance crystallizes from ligroine of boiling range 85-95°. The yield of completely pure product is 78.0% of the theoretical; m. p. 60-61°. The composition and molecular weight of the substance correspond to the formula $C_6H_5CONPCl_3$. The product readily reacts with water, alcohols and phenols. On heating, it breaks down quantitatively to phosphorus oxychloride and benzonitrile. By the action of atmospheric moisture in benzene solution, or better by the action of 1 mole anhydrous formic acid in benzene solution, it is converted in nearly quantitative yield into the chloride of benzoylamidophosphoric acid which was previously obtained by Titherley.

Consequently there is no doubt whatever that the substance in question is trichlorophosphazobenzoyl $C_6H_5CON{=}PCl_3$ or a product of its isomerization – the chloride of the N-phosphoric acid of benzimidochloride $C_6H_5CCl{=}NPOCl_2$. An isomerization of this type is not excluded since phosphorus possesses a great affinity for oxygen. The nearly theoretical yield of crude product, the closeness of the melting points of the crude and pure substances, the high yield of hydrogen chloride and the absence from the distillate of appreciable amounts of phosphorus oxychloride completely exclude Wallach's mechanism for the reaction of benzamide with phosphorus pentachloride and fully confirm the strict accuracy of our new scheme advanced above.

The question naturally arises as to why Wallach and, later, Titherley and Worrall did not obtain trichlorophosphazobenzoyl. The reason is a very simple one. Trichlorophosphazobenzoyl is obtained in nearly quantitative yield only when the mixture of phosphorus pentachloride, benzamide and carbon tetrachloride is, shortly after mixing, at once raised to at least 50-60° and after the conclusion of the reaction the solvent is immediately driven off completely in a good vacuum. If the mixture is allowed to stand at room temperature before heating or if the reaction is performed at 30° or the mixture is allowed to stand after carrying out the reaction, then the yields of trichlorophosphazobenzoyl fall sharply and its isolation becomes impossible in practice. Wallach entirely failed to detect this phenomenon. Titherley and Worrall did indeed detect it but could not find its explanation.

The explanation proved to be very simple. Hydrogen chloride has a remarkably strong catalytic effect upon the cleavage of trichlorophosphazobenzoyl into phosphorus oxychloride and benzonitrile. In the absence of hydrogen chloride the reaction proceeds rapidly and quantitatively only at above 100°. At room temperature, certainly in the absence of moisture, trichlorophosphazobenzoyl can be stored for at least several months without appreciable decomposition although a weak odor of benzonitrile is developed after only a few hours. In presence of hydrogen chloride, for example in solution in carbon tetrachloride saturated with hydrogen chloride, cleavage takes place very quickly and is nearly complete in the course of 20-30 hours at room temperature. It is interesting that phosphorus pentachloride has no catalytic action at all and in its presence (5%) no change occurs in trichlorphosphazobenzoyl in carbon tetrachloride solution at room temperature in the course of three days. Consequently, a condition for obtaining good yields of trichlorophosphazobenzoyl is to perform the reaction and isolate the products in conditions ensuring maximum speed and completeness of removal of hydrogen chloride.

It remains to clear up the problem of the structure of trichlorophosphazobenzoyl, i.e. whether or not it isomerizes in the process of formation into the chloride of the N-phosphoric acid of benzimidochloride:

$$C_6H_5CON{=}PCl_3 \;?\rightarrow\; ?\; C_6H_5CCl{=}NPOCl_2$$

A completely rigorous proof of the structure of the product of reaction of phosphorus pentachloride with benzamide can only be obtained with the help of physical methods of investigation; this will be done later. At the present time the structure of trichlorophosphazobenzoyl can be demonstrated by a chemical method.

Reaction of trichlorophosphazobenzoyl with dry sodium phenate in benzene solution at a temperature not higher than 80° gives a nearly quantitative yield of the well-crystallized triphenyl ester of benzoylimidophosphoric acid (triphenoxyphosphazobenzoyl):

$$C_6H_5CON{=}PCl_3 + 3C_6H_5ONa \rightarrow 3NaCl + C_6H_5CON{=}P(OC_6H_5)_3.$$

When distilled or when kept at room temperature for a week in presence of traces of hydrogen chloride, the triphenyl ester of benzoylimidophosphoric acid quantitatively breaks down to benzonitrile and triphenyl phosphate according

to the scheme:

$$C_6H_5CON{=}P(OC_6H_5)_3 \rightarrow C_6H_5CN + OP(OC_6H_5)_3.$$

This cleavage proves that the triphenyl ester of benzoylimidophosphoric acid and consequently also trichlorophosphazobenzoyl are indeed phosphazo compounds and not their isomers with a phenoxy group and chlorine atom at the carbon atom:

$$C_6H_5C(OC_6H_5){=}NPO(OC_6H_5)_2 \quad \text{and} \quad C_6H_5C(Cl){=}NPOCl_2,$$

since it is extremely improbable that one would obtain from $C_6H_5CCl{=}NPOCl_2$ and $3C_6H_5ONa$ at 80° the triphenyl ester of benzoylimidophosphoric acid, and also extremely improbable that in such mild conditions the phenoxy group would migrate from the carbon to the pentavalent phosphorus. Migration of an oxygen atom from carbon to phosphorus is quite often observed. Consequently we can claim that proof has been obtained, as far as this is possible by a purely chemical method, that the first product of the reaction of phosphorus pentachloride with benzamide is trichlorophosphazobenzoyl.

Wallach [2] also obtained from the amides of dichloro- and trichloroacetic acids compounds with the composition $RCONPCl_6$ to which he assigned, without any proof, the structure $RCCl{=}NPOCl_2$. Wallach explained the formation of these compounds, once again without any experimental basis, by the scheme:

$$RCONH_2 + PCl_5 \rightarrow RCCl_2NH_2 + POCl_3;$$
$$RCCl_2NH_2 \rightarrow HCl + RCCl{=}NH + HCl;$$
$$RCCl{=}NH + POCl_3 \rightarrow HCl + RCCl{=}NPOCl_2.$$

Later Steinkopf [4] obtained several analogous compounds from amides of a series of substituted acetic acids and accepted for them the structure and formation mechanism proposed by Wallach.

If Wallach's scheme were correct, then the final phosphorus compounds should have been obtained not only from phosphorus pentachloride and amides of carboxylic acids but also from imidochlorides and phosphorus oxychloride. Neither Wallach nor Steinkopf carried out such experiments. Final refutation of Wallach's scheme was obtained by numerous experiments in the most diverse conditions involving reaction of imidochlorides with phosphorus oxychloride and of nitriles with phosphorus oxychloride and hydrogen chloride. In not a single case was a trichlorophosphoacyl obtained. Consequently Wallach's scheme for the formation of phosphorus-containing products of reaction of phosphorus pentachloride with carboxylic acid amides is entirely erroneous and all the compounds of this type obtained for the reaction of benzamide with phosphorus pentachloride have been confirmed with amides of several substituted benzoic acids.

The next model substance selected for study of the reaction of phosphorus pentachloride with carboxylic acid amides was ethyl carbamate. If the reaction with ethyl carbamate proceeded according to Wallach's scheme, then the reaction products should be the corresponding amidochloride, imidochloride, ethyl cyanate and ethyl cyanurate. If the reaction proceeded with detachment of ethyl chloride, then the resultant cyanic and (later) cyanuric acid should be obtained according to the equations:

$$NH_2COOC_2H_5 \xrightarrow{+PCl_5} NH_2CCl_2OC_2H_5 \rightarrow NH{=}CClOC_2H_5;$$
$$NH{=}CClOC_2H_5 \rightarrow N{\equiv}COC_2H_5 \rightarrow C_3N_3(OC_2H_5)_3$$
$$NH{=}CClOC_2H_5 \rightarrow N{\equiv}COH \rightarrow C_3H_3(OH)_3$$

Not one of these products is actually formed. In fact the reaction proceeds according to the general scheme with nearly quantitative formation of the ethyl ester of trichlorophosphazocarbonic acid:

$$C_2H_5OCONH_2 + PCl_5 \rightarrow 2HCl + C_2H_5OCON{=}PCl_3.$$

This ester is a liquid with a pungent odor, stable at low temperatures. At 45° the ester nearly quantitatively breaks down to ethyl chloride and isocyanophosphoryl chloride according to the equation:

$$C_2H_5OCON{=}PCl_3 \rightarrow C_2H_5Cl + O{=}C{=}NPOCl_2.$$

If heating is not done carefully, the reaction takes place explosively. Isocyanophosphoryl chloride is a colorless liquid, b.p. 136-138°, with a very unpleasant odor recalling the odor of perspiration. Isocyanophosphoryl chloride is very reactive; with alcohols it gives in succession urethanphosphoryl chloride and esters of urethanphosphoric acids:

$$Cl_2PONCO + ROH \rightarrow Cl_2PONHCOOR;$$
$$Cl_2PONHCOOR + 2R'ONa \rightarrow (R'O)_2PONHCOOR,$$

with ammonia and amines it gives the corresponding derivatives of urea, etc. Consequently isocyanophosphoryl chloride may serve as a starting substance for the preparation of the most diverse derivatives of phosphoric acid.

Reaction of phosphorus pentachloride with urea led to the analog of bis-trichlorophosphazosulfone [8], namely bis-trichlorophosphazocarbonyl, m.p. 40-41°:

$$H_2NCONH_2 + 2PCl_5 \rightarrow 4HCl + Cl_3P{=}NCON{=}PCl_3$$

and high-melting products of approximately the same elementary composition which have not yet been investigated.

A study of the reaction of phosphorus pentachloride with ethyl oxamate, which had been the sole experimental basis for Wallach's theory and appeared to confirm the correctness of his proposed mechanism, likewise showed that Wallach's scheme was wrong. It was found that ethyl oxamate readily enters into reaction not only with one but also with two molecules of phosphorus pentachloride, a fact which Wallach failed to notice. The first product of the reaction is not the amidochloride but its isomer with the structure $C_2H_5OCCl_2CONH_2$ i.e. the amide of dichloroethoxyacetic acid, which is formed in a yield of about 60% according to the equation:

$$C_2H_5OCOCONH_2 + PCl_5 \rightarrow C_2H_5OCCl_2CONH_2 + POCl_3,$$

i.e. completely analogous to the esters of dichloroalkoxyacetic acids which are easily formed from esters of oxalic acid [12]:

$$C_2H_5OCOCOOC_2H_5 + PCl_5 \rightarrow C_2H_5OCCl_2COOC_2H_5 + POCl_3.$$

In the case of ethyl oxamate this reaction proceeds with even greater facility than with esters of oxalic acid.

Dichloroethoxy acetamide is a colorless, very easily crystallizing substance, completely stable at temperatures below 100° and melting at 81-82°. The amide is rather slowly decomposed by water and very closely resembles the esters of dichloroalkoxyacetic acids in all its properties. The structure of the compound is fairly rigorously proved by its great stability at room temperature as well as by the formation with alcohols, even though in low yields, of the corresponding esters of oxamic acid and not of iminoesters, according to the scheme:

$$NH_2COCCl_2OC_2H_5 + ROH \rightarrow NH_2COCOOR + C_2H_5Cl + HCl;$$
$$C_2H_5OCOCCl_2NH_2 + ROH ? \rightarrow ? C_2H_5OCOC(OR){=}NHHCl + HCl$$

also by the fact that with alkoxides it gives good yields of amides of the half orthoesters of oxalic acid (amides of trialkoxyacetic acids), according to the reaction:

$$NH_2COCCl_2OR + 2R'ONa \rightarrow 2NaCl + NH_2COC(OR')_2(OR).$$

One compound of this type described in the literature is the amide of the half orthomethyl ester of oxalic acid, obtained from the methyl ester of trimethoxyacetic acid and ammonia [13]. The product obtained from the admie of dichloromethoxyacetic ester and sodium methoxide

$$NH_2COCCl_2OCH_3 + 2CH_3ONa \rightarrow 2NaCl + NH_2COC(OCH_3)_3$$

proved to be identical with the compound described in the literature.

The preparation in good yields of amides of dichloroalkoxyacetic acids simply and naturally explains why Wallach obtained esters of oxamic acid from "amidochlorides" of ethyl oxamate and alcohols (see above). The simple explanation is that the "amidochloride" of Wallach did not contain any amidochloride but contained the amide of dichloroethoxyacetic acid.

The second product of reaction of phosphorus pentachloride with ethyl oxamate is trichlorophosphazo-dichloroethoxyacetyl, formed almost quantitatively according to the equation:

$$C_2H_5OCOCONH_2 + 2PCl_5 \rightarrow C_2H_5OCCl_2CON{=}PCl_3 + 2HCl + POCl_3$$

The same product may be obtained from dichloroethoxyacetamide and one molecule of phosphorus pentachloride. Trichlorophosphazo-dichloroethoxyacetyl is a colorless crystalline compound with m.p. 71-72°, perfectly stable at room temperature; its structure is proved by the method of preparation, by the almost theoretical yields of all the products of the reaction, by the elementary composition, by the molecular weight and by its chemical properties.

Under the action of water vapor in benzene solution, or better by the action of one molecule of anhydrous formic acid, trichlorophosphazodichloroethoxyacetyl is converted in nearly quantitative yield into dichloroethoxy-

acetylamidophosphoryl chloride:

$$C_2H_3OCCl_2CON{=}PCl_3 + HCOOH \rightarrow HCl + CO + C_2H_3OCCl_2CONHPOCl_2.$$

The composition and properties of this substance correspond to the very same product that Wallach isolated from the product of reaction of phosphorus pentachloride with ethyl oxamate after exposure to atmospheric moisture. Consequently, the formation of this substance cannot be reconciled at all with a reaction of an imidochloride with phosphorus oxychloride under the influence of atmospheric moisture, as Wallach had thought, nor with the fact that the trichlorophosphazodichloroethoxyacetyl present in the reaction mixture was hydrolyzed at the first step and gave the considerably more stable dichloroethoxyacetylamidophosphoryl chloride which Wallach was able to isolate in the pure form and to analyze. Trichlorophosphazodichloroethoxyacetyl reacts readily with water, alcohols, phenols, ammonia and amines, just like other trichlorophosphazo compounds. Hence the reaction of ethyl oxamate with phosphorus pentachloride proceeds according to the general scheme but is accompanied by a reaction similar to that of phosphorus pentachloride with esters of oxalic acid.

A close examination of the experimental part of Wallach's paper reveals why he failed to isolate even a single product of the direct interaction of phosphorus pentachloride with ethyloxamate in the pure form. First, as indicated above, Wallach did not observe that ethyl oxamate readily reacts not only with one molecule but also with two molecules of phosphorus pentachloride. This oversight prevented him from deliberately selecting the most suitable conditions for the formation of one or the other substance and resulted in the reaction product always being a difficultly resolvable mixture. Second, , the paper teems with fundamental experimental errors, of which the most important were the following: Wallach "dried" and stored all his substances in desiccators over soda lime or calcium chloride, which was most unwise because the vapor tension of water over these agents is fairly considerable at room temperature, while the vapor tension of water vapor over the products of reaction of ethyl oxamate with phosphorus pentachloride is substantially zero. In other words, Wallach dried the soda lime and calcium chloride with the substances which he had prepared; the latter naturally then hydrolyzed withevolution of hydrogen chloride which reacted with soda lime to produce more water; the latter again reacted with the substances, and so on. The next fundamental error was the lack of quantitative check of the reactions in progress by quantitative determination of the evolved hydrogen chloride and phosphorus oxychloride, which could have been easily effected. Thus, for example, calculation of the amount of hydrogen chloride permits an assessment of the extent to which the reaction proceeds with formation of trichlorophosphazo compound, and calculation of the amount of phosphorus oxychloride permits an assessment of the extent of replacement of oxygen by two atoms of chlorine. These and other experimental defects resulted in Wallach's failure to isolate in the pure form the products of a reaction which proceeds substantially quantitavely; this circumstance retarded for many years the development of this branch of the chemistry of the carboxylic acid amides.

The detailed experimental data and a detailed account of the properties of thecompounds discussed and of analogous compounds will be submitted in a series of papers.

SUMMARY

1. The scheme of Wallach for the reaction of unsubstituted carboxylic acid amides with phosphorus pentachloride, generally accepted at the present day, is erroneous. Amidochlorides are not formed in the action of phosphorus pentachloride on unsubstituted carboxylic acid amides.

2. The reaction of unsubstituted amides of carboxylic acids with phosphorus pentachloride actually proceeds with formation of trichlorophosphazoacyls and two molecules of hydrogen chloride.

3. When heated or when exposed to the catalytic action of hydrogen chloride at room temperature, trichlorophosphazoacyls break down to phosphorus oxychloride and nitriles.

4. The structure of the produt of reaction of phosphorus pentachloride with benzamide was established as that of trichlorophosphazobenzoyl by a chemical method.

5. Trichlorophosphazoacyls are extremely reactive and can serve as starting substances for the preparation of the most diverse derivatives of phosphoric acid.

6. Reaction of phosphorus pentachloride with ethyl carbamate gives the ethyl ester of trichlorophosphazocarbonic acid which at 45° cleaves to ethyl chloride and isocyanophosphoryl chloride.

7. Reaction of phosphorus pentachloroide with ethyl oxamate gives at first dichloroethoxyacetamide and then trichlorophosphazo-dichloroethoxyacetyl.

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Received April 27, 1954

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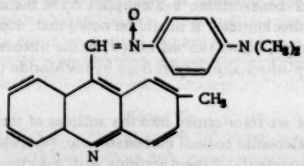
CONDENSATION OF BENZO DERIVATIVES OF 9-METHYLACRIDINE

III. CONDENSATIONS WITH p-NITROSODIMETHYLANILINE

B. M. Mikhailov and G. S. Ter-Sarkisyan

In the previous communications [1,2] it was shown that in passing from 9-methylacridine to its mono- and dibenzo derivatives, the activity of the methyl group is lowered in reactions with aromatic aldehydes and nitroso and diazo compounds. In the present communication we submit the results of an investigation of condensations of 9-methylacridine, 9-methyl-1,2-benzacridine*, 9-methyl-1,2,7,8-dibenzacridine, also of 4-methyl-5,6-benzoquinoline* and 4-methyl-7,8-benzoquinoline, with p-nitrosodimethylaniline in various conditions. The investigation was undertaken with the aim of establishing the activity of the methyl groups of these compounds in dependence on the number and position of the benzene rings in the molecule.

As we know, 9-methylacridine reacts with facility with aromatic nitroso compounds when the starting substances are heated in presence of sodium carbonate or hydroxide, forming the corresponding nitrones and azomethines [3,4,5] whereas α-picoline, quinaldine and lepidine only enter into this reaction in the form of quaternary salts [6]. It was found that 4-methyl-5,6-benzoquinoline, 4-methyl-7,8-benzoquinoline, 9-methyl-1,2-benzacridine and 9-methyl-1,2,7,8-dibenzacridine likewise do not react with p-nitrosodimethylaniline when alcoholic solutions of the components are heated in presence of alkaline catalysts. On the other hand, as our experiments showed, 9-methylacridine condenses with p-nitrosodimethylaniline even at room temperature and in the complete absence of condensing agents. This once again emphasizes the great mobility of the hydrogen atoms of the methyl group of 9-methylacridine in comparison with all the remaining compounds investigated. Also proceeding with ease is the reaction between 2,9-dimethylacridine and p-nitrosodimethylaniline with formation of α-9(2-methylacridyl)-N-(p-dimethylaminophenyl)-nitrone (I):

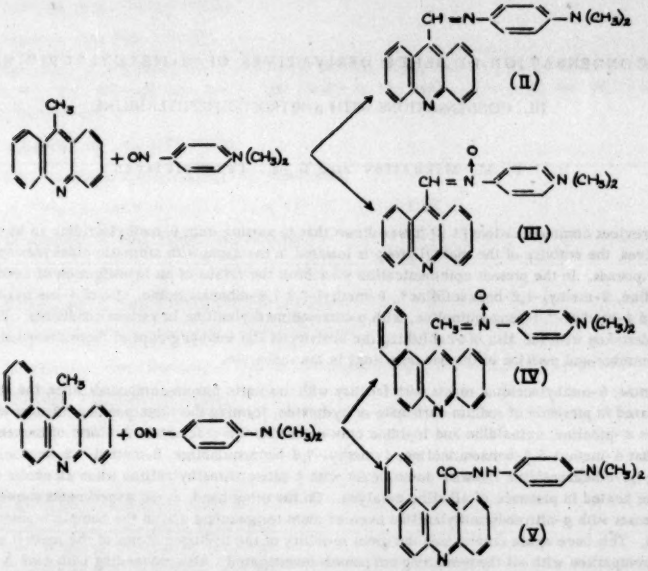


(I)

Study of the photochemical condensations of the above-mentioned compounds with p-nitrosodimethylaniline showed that these reactions could not be effected for 5,6- and 7,8-benzo derivatives of lepidine even under the influence of ultraviolet rays. Only 9-methylacridine and 9-methyl-1,2-benzacridine entered into reaction with p-nitrosodimethylaniline on irradiation of the alcoholic solutions of the starting substances with a PRK-2 quartz mercury lamp; in the first case a mixture of the p-dimethylaminoanil of acridine-9-aldehyde (II) and α-9-acridyl-N-p-dimethylaminophenylnitrone (III) was obtained; in the second case a mixture of α-(1,2-benzacridyl-9)-N-(p-dimethylaminophenyl)-nitrone (IV) and the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid (V): (See page 560).

It is possible that the anilide (V) is obtained by isomerization of the nitrone (IV) under the action of ultraviolet rays. A similar isomerization of α-N-9-acridylphenylnitrone into the anilide of acridine-9-carboxylic acid under the action of sunlight was previously observed by Chardonnens [5].

* Publisher's note: The Russian convention for numbering of benzacridines, etc. differs from that adopted by Chemical Abstracts.



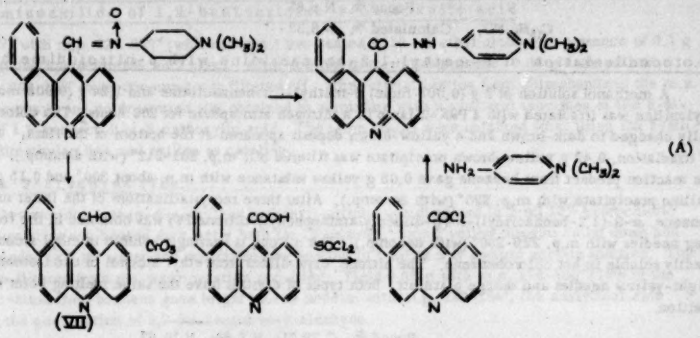
We also observed the formation of the nitrone (IV), the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid (V) and the p-dimethylaminoanil of 1,2-benzacridine-9-aldehyde (VI) in the condensation of 9-methyl--1,2-benzacridine with p-nitrosodimethylaniline hydrochloride. It should be noted that, depending upon the ratios of starting materials and the duration of the experiment, either the anilide (V) or the nitrone (IV) will preponderate in the reaction products; with increasing amount of p-nitrosodimethylaniline hydrochloride the yield of nitrone falls and that of the anilide rises.

It is known that nitrones of the aromatic series are transformed into the anilides of the corresponding acids under the influence of acetic anhydride, acetyl chloride, alcoholic sodium carbonate, etc. [7,8,9]. On the basis of results that we obtained in a study of the condensation of 9-methyl-1,2-benzacridine with p-nitrosodimethylaniline hydrochloride, we suggested that the anilide (V) is a product of isomerization of the nitrone (IV) under the action of the hydrochlorides of the initial or intermediate products of the reaction.

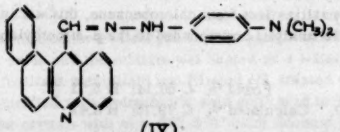
Special experiments on the isomerization of α-1,2-benzacridine-9-N-(p-dimethylaminophenyl)-nitrone (IV) under the influence of amine salts (hydrochlorides of p-nitrosodimethylaniline and aniline) confirmed this suggestion. In all cases the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid was isolated. The structure of the latter was confirmed by synthesis from p-dimethylaminoaniline and 1,2-benzacridine-9-carboxylic acid chloride. This acid, in turn, was obtained by oxidation of 1,2-benzacridine-9-aldehyde (VII), which is formed by hydrolysis of the nitrone (IV) with weak hydrochloric acid. The following series of transformations was thus realized: (See A, page 561).

It may be noted that hydrolysis of the nitrone (I) gave 2-methylacridine-9-aldehyde (VIII).

9-Methyl-1,2-benzacridine, like 9-methyl-3,4-benzacridine [5], couples with p-nitrodiazobenzene, but unlike 9-methylacridine it does not react with diazobenzene, whereas 9-methyl-1,2,7,8-dibenzacridine does not react with either of these diazo compounds. The reaction between 9-methyl-1,2-benzacridine and p-nitrophenyldiazonium proceeds in a medium of glacial acetic acid with formation of compound (IX) which has the structure of the p-nitrophenylhydrazone of 1,2-benzacridine-9-aldehyde: (see B, page 561).



(A)



(B)

(IX)

EXPERIMENTAL

Condensation of 9-methylacridine with p-nitrosodimethylaniline

a) Under the action of ultraviolet rays. A methanol solution of 3 g (0.015 mole) 9-methylacridine and 2.31 g (0.015 mole) p-nitrosodimethylaniline was irradiated in a molybdenum glass flask with a PRK-2 lamp. After 21 hours' irradiation, 2.78 g brown crystalline precipitate with m.p. 233-243° was obtained. Irradiation for a further 50 hours gave a further 1.01 g product with the same m.p. Crystallization from chlorobenzene gave 1.61 g (44.7% of the theoretical) of α-9-acridyl-N-(p-dimethyl-aminophenyl)-nitrone (III) with m.p. 234-235.5° (with decomposition).

Found %: C 77.39; H 5.73.

$C_{22}H_{19}N_3O$. Calculated %: C 77.39; H 5.61.

and 0.7 g (yield 14% of the theoretical) of dark violet crystals of the p-dimethylaminoanil of 9-acridinealdehyde (II) with m.p. 248-249° Chardonnens gives m.p. 243° for the nitrone (III) and m.p. 248° for the azomethine (II).

b) In the dark at room temperature. A methanol solution of 2 g 9-methylacridine and 1.59 g p-nitrosodimethylaniline was left in the dark at room temperature. After 21 days 2.54 g of a mixture of substances was obtained (71% of the amount of starting materials), and after crystallization from chlorobenzene gave 1.14 g of nitrone (III) with m.p. 235.5° (with decomp.) and 0.39 g azomethine (II) with m.p. 248-249°.

α-(2-Methyl-9-acridyl)-N-(p-dimethylaminophenyl)-nitrone (I)

0.5 g (0.0024 mole) 2,9-dimethylacridine and 0.36 g (0.0024 mole) p-nitrosodimethylaniline were dissolved in 10 ml methanol. To the solution was added 3 drops conc. sodium carbonate solution and the mixture heated under a reflux condenser for 5 hours. After cooling, 0.22 g dark-cherry precipitate with m.p. 215-220° was filtered from the solution. After crystallization from dioxane, xylene and ethyl acetate, α-(2-methyl-9-acridyl)-N-(p-dimethylaminophenyl)-nitrone formed lustrous, dark-red crystals with m.p. 224-225°.

Found %: C 77.49; H 5.85; N 12.11

$C_{23}H_{21}N_3O$. Calculated %: C 77.72; H 5.95; N 11.82

2-Methylacridine-9-aldehyde (VIII)

0.22 g α-(2-methyl-9-acridyl)-N-(p-dimethylaminophenyl)-nitrone was dissolved in 10 ml 5% hydrochloric acid at room temperature. A yellow precipitate of 2-methylacridine-9-aldehyde hydrochloride rapidly came down. It was filtered, shaken with water and neutralized with a few drops of ammonia. Yield 0.11 g with m.p.

about 130°. After crystallization from ligroine, 2-methylacridine-9-aldehyde formed yellow crystals with m.p. 136-138°. Readily soluble in the common organic solvents.

Found %. N 6.61
$C_{15}H_{11}NO$. Calculated %. N 6.33

Photocondensation of 9-methyl-1,2-benzacridine with p-nitrosodimethylaniline

A methanol solution of 2 g (0.008 mole) 9-methyl-1,2-benzacridine and 1.24 g (0.008 mole) p-nitrosodimethylaniline was irradiated with a PRK-2 lamp in a nitrogen atmosphere for 200 hours. The color of the solution gradually changed to dark-brown and a yellow-brown deposit appeared at the bottom of the flask. After the completion of irradiation, 0.42 g yellow-brown precipitate was filtered off; m.p. 201-212° (with decomp.). Crystallization of the reaction product from benzene gave 0.05 g yellow substance with m.p. about 300° and 0.15 g yellow-orange crystalline precipitate with m.p. 223° (with decomp.). After three recrystallizations of the latter substance from chlorobenzene, α-9-(1,2-benzacridyl)-N-(p-dimethylaminophenyl)-nitrone(IV) was obtained in the form of bright-yellow, long needles with m.p. 229-230° (with decomp.). The nitrone is sparingly soluble in ethyl alcohol and benzene, readily soluble in hot chlorobenzene. The nitrone crystallizes from ethyl alcohol in two isomorphic forms — small, bright-yellow needles and orange platelets. Both types of crystals have the same melting point and elementary composition.

Found %. C 79.71; H 5.64; N 10.67
$C_{26}H_{21}N_3O$. Calculated %. C 79.75; H 5.41; N 10.73

Evaporation of the primary alcoholic mother liquor to half its volume led to separation of the substance with m.p. approx. 300°; after two crystallizations from chlorobenzene, this was in the form of fine, yellow needles with m.p. 290-291° (with decomp.); its analysis corresponded to the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid

Found %. C 80.14; H 5.71
$C_{26}H_{21}N_3O$. Calculated %. C 79.75; H 5.41

A mixture with a synthetic specimen of the same anilide did not give a depression of m.p.

Condensation of 9-methyl-1,2-benzacridine with p-nitrosodimethylaniline hydrochloride.

a) Into a hot ethanol solution of 1 g (0.004 mole) 9-methyl-1,2-benzacridine was introduced 0.6 g (0.0032 mole) p-nitrosodimethylaniline hydrochloride; the mixture was then heated for 15 minutes. At the end of the heating the solution deposited long yellow needles which were filtered, washed with ethyl alcohol and dried (0.51 g, m.p. 216-220° with decomp.). After two crystallizations from chlorobenzene the substance had m.p. 225-227° (with decomp.) and was α-9-(1,2-benzacridyl)-N-(p-dimethylaminophenyl)-nitrone (IV). A mixed sample with the nitrone obtained by photocondensation did not give a depression of m.p. On diluting the original mother liquor with water and crystallizing the resultant precipitate from ethyl alcohol, 0.08 g p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid was obtained; m.p. 277-280° (with decomp.). The following were also obtained from the liquor: 0.12 g nitrone with m.p. 210-216° and 0.27 g of the original 9-methyl-1,2-benzacridine with m.p. 140-144°.

b) In an experiment with the same ratio of components and 3 hours' heating, 1.2 g 9-methyl-1,2-benzacridine yielded 0.4 g p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid with m.p. 288-290° (with decomp.). On dilution of the primary mother liquor and recrystallization of the resultant precipitate from ethyl alcohol, a further 0.5 g p-dimethylaminobenzanilide of 1,2-benzacridine-9-carboxylic acid, m.p. 267-275° (with decomp.) was obtained, together with 0.16 g of a substance with m.p. 159-164° which after two recrystallizations from the same solvent was isolated in the form of yellow-orange needles with m.p. 168-169° and whose analysis corresponded to that of the p-dimethylaminoanil of 1,2-benzacridine-9-aldehyde (VI)

Found %. C 83.30; H 5.78
$C_{28}H_{21}N_3$. Calculated %. C 83.17; H 5.64

The azomethine (VI) is more soluble in ethyl alcohol and benzene than is its corresponding nitrone (IV). Gentle heating of a solution of the azomethine with dilute hydrochloric acid in presence of phenylhydrazine hydrochloride leads to a copious violet precipitate of the phenylhydrazone of 1,2-benzacridyl-9-aldehyde.

c) As a result of doubling the amount of p-nitrosodimethylaniline hydrochloride and a 15 minutes' duration of the experiment, from 0.5 g 9-methyl-1,2-benzacridine and 0.6 g p-nitrosodimethylaniline hydrochloride was obtained 0.43 g crystalline precipitate with m.p. 262-275° (with decomp.); this was recrystallized from glacial acetic acid and then from chlorobenzene, giving the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid with m.p. 288-290° (with decomp.) (mixed test).

Isomerization of α-9-(1,2-benzacridyl)-N-(p-dimethylaminophenyl)-nitrone into the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid

0.1 g nitrone (IV) with m.p. 225-227° (with decomp.) was heated in 10 ml ethyl alcohol in presence of 0.1 g 9-methyl-1,2-benzacridine hydrochloride for 3 hours. After cooling to room temperature, 0.04 g dark-yellow, fine crystals with m.p. 272-282° (with decomp.) was filtered off. After crystallization from chlorobenzene the m.p. was 282-286° (with decomp.), and no depression was obtained in admixture with a synthetic specimen of the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid. The same results were obtained when using the hydrochlorides of p-nitrosodimethylaniline and aniline as catalysts.

1,2-Benzacridine-9-aldehyde (VII).

0.1 g α-9-(1,2-benzacridine)-N-(p-dimethylaminophenyl)-nitrone was dissolved in 2 ml 10% hydrochloric acid. The transparent solution was heated on a water bath for 15 minutes. Small yellow needles came down and were filtered off, suspended in 7 ml water and neutralized by heating in 1 ml of 2 N sodium acetate solution. The product of reaction was filtered from the warm solution and dried. Yield 0.05 g with m.p. 176-180° (76% of the theoretical). Crystallization from benzene gave bright yellow needles with m.p. 183-184°, the analytical data for which agreed with the composition of 1,2-benzacridine-9-aldehyde

	Found %.	C 84.02; H 4.35
$C_{18}H_{11}NO$.	Calculated %.	C 84.03; H 4.31

1,2-Benzacridine-9-carboxylic acid

To a warm solution of 0.18 g 1,2-benzacridine-9-aldehyde in 5 ml glacial acetic acid was gradually added an acetic acid solution of 0.07 g chromic oxide and the mixture was heated on a water bath for 1.5 hours. The warm reaction mass was poured into water, the resultant precipitate was filtered off, treated with dilute ammonia and again filtered. The alkaline filtrate was acidified with hydrochloric acid until acid to Congo. The separated 1,2-benzacridine-9-carboxylic acid formed yellow crystals with m.p. 267-270° (with decomp.). Yield 0.066 g or 31.4% of the theoretical. The literature gives m.p. 276° (with decomp.) [10].

p-Dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid

A mixture of 0.13 g 1,2-benzacridine-9-carboxylic acid and 2.6 ml thionyl chloride was heated until the acid had completely dissolved. After driving off the excess of thionyl chloride, the yellow precipitate was heated on a water bath with 0.4 g freshly prepared p-dimethylaminoaniline for ½ hour and then treated with water containing a little ammonia. The obtained precipitate (0.13 g) crystallized from chlorobenzene in the form of fine yellow needles of the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid with m.p. 288-290° (with decomp.). The compound is poorly soluble in common organic solvents and differs from the nitrone (IV) in not being hydrolyzed by weak acids with formation of 1,2-benzacridine-9-aldehyde.

Coupling of 9-methyl-1,2-benzacridine with p-nitrodiazobenzene

0.5 g (0.002 mole) 9-methyl-1,2-benzacridine was dissolved in 15 ml glacial acetic acid. To the solution was added 1.5 g sodium acetate followed, with constant stirring, by 1.5 ml aqueous solution of p-nitrodiazobenzene (prepared by the usual method). On addition of the first few drops of diazo compound the color of the solution changed from light-yellow to cherry red and a dark, amorphous precipitate then came down. The following day 0.66 g of the dark-cherry salt of the dye was filtered off. The base was obtained by heating the salt with dilute ammonia. Yield 0.46 g in the form of yellow-orange crystals with m.p. approx. 300° (yield 57.5% of theoretical).

After many recrystallizations from xylene and then from benzene polychlorides, the compound formed fine plates with m.p. 262.5-264.5°. The compound is sparingly soluble in common organic solvents, readily soluble in pyridine.

	Found %.	C 73.20; H 4.03
$C_{24}H_{16}N_4O_2$	Calculated %.	C 73.45; H 4.11

SUMMARY

1. 9-Methylacridine is able to condense with p-nitrosodimethylaniline in the dark, at room temperature and without the presence of any catalysts. This reaction proceeds at a much greater velocity under the influence of ultraviolet rays.

2. 9-Methyl-1,2-benzacridine condenses with p-nitrosodimethylaniline when irradiated with ultraviolet light and forms α-9-(1,2-benzacridine)-N-(p-dimethylaminophenyl)-nitrone and the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid.

3. Condensation of 9-methyl-1,2-benzacridine with the hydrochloride of p-nitrosodimethylaniline leads to three substances: p-dimethylaminoanil-1,2-benzacridine-9-aldehyde (VI), α-9-(1,2-benzacridyl)-N-(p-dimethylaminophenyl)-nitrone (IV) and the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid (V). The nitrone (IV) undergoes rearrangement into the anilide (V) under the action of amine salts.

4. 9-Methyl-1,2-benzacridine does not react with diazobenzene but couples with p-nitrodiazobenzene in glacial acetic acid.

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Received June 23, 1953

HIGH MOLECULAR COMPOUNDS

64. THE POLYCONDENSATION OF THE ETHYL ESTER OF D,L-ALANINE

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Although α-amino acids are readily available substances, many of their transformations and, in particular their polycondensations, have been very little studied. The literature contains only a few reports of experiments on the heating of the amino acids themselves or of their esters with formation of the corresponding polyamides and diketopiperazines.

Thus Curtius [1] and Fischer [2] gave a number of examples in illustration of the ability of esters of α-amino acids to form both linear polymers and cyclic dimers (diketopiperazines). Frenkel and Katchalski [3], and later Pacsu [4] carried out polycondensations of esters of α-amino acids. Frenkel and Katchalski obtained linear polymers with a polymerization coefficient of 14 to 110.

Polyakova and Vereshchagin [5] observed the influence of pressure on the formation of polypeptide chains. Bresler and Glikina [6] showed that alanine ester in aqueous solution under a pressure of 5000 atm, forms a diketopiperazine, while trialanine ester forms a polymer with a polymerization coefficient of 12-15.

We have studied the polycondensation of the ethyl ester of D,L-alanine in various temperature conditions with special reference to the clarification of the effect of catalysts on this reaction.

We prepared the starting ethyl ester of D,L-alanine by Fischer's method [7] and finally purified it by vacuum distillation in carbon dioxide-free air in the special apparatus described below.

EXPERIMENTAL PROCEDURE

We established that carbon dioxide is an extremely active catalyst for the polycondensation of alanine ester, and this necessitated the preparation of the starting material and the performance of the polycondensation reaction itself in conditions ensuring complete absence of carbon dioxide; it was necessary to have a method of exact proportioning of the minute amounts of carbon dioxide employed as catalyst. The polycondensation reaction was therefore performed in sealed ampoules heated in a thermostat at 55 ± 0.1°. The ampoules were filled in the apparatus sketched in Fig. 1 which permitted preparation of carbon dioxide-free ester and the proportioning of small additions of carbon dioxide and other catalysts.

The apparatus consists of a flask A, equipped with a condenser joined through a ground-glass connection with a chamber B, whose side tubes are joined by ground-glass connections to a round-bottomed flask O and special receivers for weighed amounts of ester; the shape of these receivers varies with the nature of the catalyst. When the catalyst is carbon dioxide the receiver sketched in more detail in Fig. 2 is used, while in the case of other catalysts the simpler receiver illustrated in Fig 3 is used.

When carrying out the polycondensation reaction in presence of carbon dioxide, the gas buret E is first filled with carbon dioxide via the limb F while the tap K is closed and tap L is open. The apparatus is then pumped out with a vacuum pump to a residual pressure of 2-3 mm and again filled with dry carbon dioxide which had been dried over sulfuric acid. The carbon dioxide is derived from chemically pure sodium bicarbonate and sulfuric acid. These operations are repeated six times and dry nitrogen is passed through after filling of the buret with carbon dioxide and closing tap L and limb F. After this the apparatus for proportioning the carbon dioxide is weighed on an analytical balance.

The apparatus set up in this manner (see Fig.2) is joined by ground-glass connection to the bulb C to which is attached the condenser (see Fig. 1). In the distillation flask A is placed 1 to 1,5 g freshly prepared alanine ester which had been dried over dry potassium carbonate; the ester is distilled in vacuum (2-4 mm). The ethyl ester of alanine, coming over at 26-30°, enters the receiver C and is run into ampoule D. After 20-25 drops of the ester had collected in the receiver, the bulb B is switched round and the remaining ester is collected in flask O. While the vacuum pump is running, the receiver C is sealed off from the remainder of the proportioning system. The receiver C is then removed with the bulb B, the ground-glass joint being carefully cleansed from vacuum grease, and weighed on an analytical balance together with the rest of the proportioning apparatus. To the difference between the weights is added the weight of the air in the ampoule, and the result is the weight of the ester (usually 0.2-0.4 g). The branch F is then filled with sulfuric acid; with tap K opened,

through tap K is introduced the required amount of carbon dioxide. Tap K is closed and ampoule D is sealed from the buret E at the point N A sealed ampoule G is thus obtained which contains a weighed amount of ester and a known amount of carbon dioxide as catalyst. The ampoule is at once placed in the thermostat and heated for the required period.

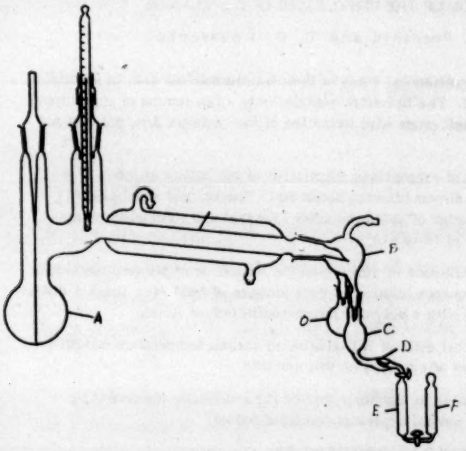

Fig. 1

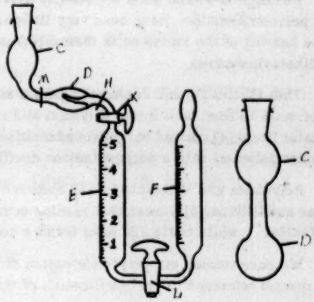

Fig. 2

Fig. 3

In experiments carried out with other catalysts, the fitment shown in Fig. 3 is used; into the latter is previously introduced the required amount of catalyst; then the required amount of ester is distilled into it and the vessel is sealed off under vacuum at point M.

After the heating, the ampoule is withdrawn from the thermostat, rapidly cooled, and crushed in a small, strong porcelain beaker to which is previously added 10-20 ml of 3% aqueous acetic acid. The resultant solution is poured into a measuring flask; the beaker is rinsed out with fresh portions of acetic acid which are also transferred to the flask; the volume is then made up to the mark with additional 3% acetic acid solution. The content of free amino groups in the solution is then determined by the Van Slyke method [8].

A series of experiments in which the reaction products were dissolved in water showed that the polycondensation reaction also takes place in aqueous solution, whereas dissolution in acetic dilute acid leads to complete stoppage of the polycondensation reaction and ensures more correct results. The polyalanine and diketopiperazine resulting from the reaction dissolve completely in 3% acetic acid as well as in water at any degree of completeness of the process, whereas the polymers obtained by heating D,L-valine, D,L-norleucine or glycine only dissolve up to the stage of 30-50% completion of the reaction. Their further heating leads to products with ever decreasing solubility in water and dilute acetic acid; their investigation therefore calls for a special technique whereas in the case of alanine such difficulties do not arise.

Water soluble products can be obtained by simultaneous polycondensation of two amino acid esters. Thus the separate heating of the ethyl esters of D,L-phenylalanine and glycine leads to water-insoluble polymers, whereas their joint polycondensation leads to formation of water-soluble products.

EXPERIMENTAL RESULTS

Investigation of the action of various additives on the reaction of polycondensation of the ethyl ester of D,L-alanine showed that considerable catalytic activity is manifested by acids such as carbonic, hydrochloric, sulfuric, acetic and propionic acids, as well as by polyalanine and aminoenanthic acid. Neutral and alkaline substances, such as diketopiperazine (lactimide), polyalanine ester, water, D,L-alanine, ammonia, diethylamine and KOH, do not bring about an appreciable increase in reaction velocity. Bearing in mind that esters of amino acids are them-

selves alkaline substances, it is clear that addition of amines and other bases cannot have an appreciable effect.

The catalysts which were most closely studied were carbon dioxide, acetic acid and polyalanine. In Table 1 are set forth the results of experiments on the polycondensation of the ethyl ester of D,L-alanine in presence of different amounts of carbon dioxide as a function of time at 55°, based on the change of content of free amino nitrogen as determined by the Van Slyke method and expressed as percentages of the original amino group content.

TABLE 1

Change of Content of Free Amino Groups in Percentages of the Original Content on Heating the Ethyl Ester of D, L-Alanine at 55° in Presence of Carbon Dioxide.

Duration of heating in hours	Amount of added carbon dioxide, in wt. %					
	0.5	1.0	1.5	2.0	3.0	4.0
1	–	–	–	89.5	–	–
2	–	–	89.0	75.7	81.0	–
3	–	86.4	–	–	69.5	67.9
4	86.8	83.2	81.5	67.3	67.0	–
5	–	–	78.3	63.6	66.8	–
6	–	79.0	–	61.3	62.5	–
7	82.0	76.0	70.5	63.2	62.4	–
8	81.2	75.7	65.5	60.6	–	–
9	–	69.7	65.6	57.4	60.0	48.3
10	–	–	63.9	51.5	50.7	42.2
11		66.8	62.7	48.0	48.7	–
15	78.8	62.9	50.5	44.9	44.8	39.9

The result of polycondensation of the ester of D, L-alanine in presence of acetic acid and polyalanine are set forth in Table 2. This table also contains for comparison the results of polycondensation of this ester without catalysts. The acetic acid and polyalanine were used in the amount of 3%. Polyalanine was prepared by hydrolysis of its ethyl ester which had been obtained by polycondensation of the ethyl ester of D,L-alanine by heating in water at 80° for 20-30 minutes. The hydrolysis led to removal of a proportion of the ester groups with formation of terminal carboxyl groups. Such a polyalanine is essentially a high-molecular carboxylic acid and it is therefore not suprising that it should resemble acetic acid in its action. For comparison Table 2 also contains the results of experiments on the polycondensation of the ethyl ester of D, L-alanine in the absence of catalysts.

TABLE 2

Change of Content of Free Amino Groups as Percentage of the Original Content on Heating the Ethyl Ester of D,L-Alanine at 55° in Presence of Acids.

Duration of heating in hours	Name of catalyst		
	Acetic acid	Polyalanine	Without catalyst
3	74.7	72.0	–
4	–	–	98.4
6	68.5	67.4	–
7	66.0	65.5	–
8	–	–	97.7
10	60.2	62.8	95.6
13	52.1	61.7	–
15	–	–	97.4

It should be pointed out that in the first stages of the polycondensation, the polymers formed are soluble in the ethyl ester of D,L-alanine and the start of precipitation of the solid phase is the instant at which 75-80% of the original free amino groups are still intact (in the temperature range of 20-100°). On the basis of this observation, we can approximately estimate the velocity of the reaction resulting from the presence in the reaction mixture of a definite amount of catalyst. It was found that at 98° in the absence of catalysts, precipitation of solid phase only commences after 28 hours, whereas in presence of 2% carbon dioxide precipitation starts after 20 minutes. In this case, therefore, there is a 93-fold increase in reaction velocity.

As we have already indicated, the reaction products separate as solids which gradually fill the whole ampoule. After opening the ampoule and removing the alcohol in vacuum at room temperature, the reaction product is a brittle mass readily

pulverizable to a fine powder which melts at 260-280° with decomposition even in a sealed capillary. The polymers give the biuret reaction (red, blue and violet) and react with picric acid. It may be mentioned that when the polycondensation is performed in an aqueous medium, products are formed which give a red-violet biuret reaction, indicating the presence of a mixture of peptides of trimers and higher orders.

The ratio between the quantitites of linear polymer and cyclic dimer was determined in several reactions by sublimation in vacuum (0.1 mm) at 140°, as well as by ionophoresis by the method of Gavrilov and Balabukha [9]. It was found that the reaction temperature has the greatest influence upon the content of cyclic dimer in the reaction mass. Thus, in polycondensations performed at 55°, the dimer content as determined by the sublimation method was 35-40%, while at 100° it reached 70-80%. Determination by the ionophoresis method gives a lower content; thus, analysis of the product obtained at 55° by this method gave a value of only 26% dimer. This low value is possibly associated with thermal destruction of the polymer during sublimation of the dimer, leading to supplementary formation of cyclic dimer.

The occurrence of a catalytic action by carbon dioxide during polycondensation of esters of α-amino acids must be taken into account in connection with their storage. Thus, in a sealed ampoule filled in a carbon dioxide-free atmosphere, the ethyl ester of D, L-alanine is kept without appreciable change for up to two months, whereas in ampoules sealed in presence of air without special precautions, already on the fifth day the separation of solid is observed. The catalytic action of traces of carbon dioxide of the air is the cause of the instability of esters of α-amino acids in storage which has been noted by many authors and which had been attributed to the spontaneous tendency to polycondensation [2]. On the basis of our data, we may say that in the complete absence catalysts, the esters of α-amino acids can be kept unchanged for an unlimited period if kept out of contact with the air.

EVALUATION OF THE RESULTS OBTAINED

The considerable acceleration of polycondensation of esters of α-amino acids caused by acidic catalysts is of great interest in opening up new perspectives in the investigation of this type of reaction. Closer consideration of the experimental results, which are plotted in Fig. 4, enable us to see that the various catalysts differ slightly from one another in activity. Thus, carbon dioxide in the amount of 2% has a greater effect that 3% acetic acid. The amount of catalyst also influences the result. With increasing amount of carbon dioxide (this aspect was studied in more detail with this catalyst) the speed of transformation increases as shown in Fig. 4, where the top curve represents the velocity of the reaction without a catalyst. The optimum amount of carbon dioxide is evidently of the order of 2%. Further increase in the amount of carbon dioxide accelerates the reaction to a considerably smaller degree. The amount of combined amino groups, however, increases particularly sharply when the duration of the polycondensation is increased, as shown in Fig. 5 where the change in the amount of combined amino nitrogen is plotted as a function of the amount of carbon dioxide used in various periods of interaction.

The catalytic action of acidic catalysts is evidently associated with their ability to yield hydrogen ions which activate the ester bond and render it more reactive. As we know, the ester bond is extremely sensitive to the action of both acidic and alkaline catalysts, in whose presence all exchange reactions at ester bonds are sharply accelerated, as one of us showed in collaboration with Vinogradova [10]. In this connection it was established that acidic catalysts are more effective than alkaline catalysts. Since esters of α-amino acids are themselves strong bases, it is not surprising that in this case other bases do not exert an appreciable effect. At the same time the strong catalytic action of acids is understandable in view of their activation of the ester bond in esters of α-amino acids.

In this connection carbon dioxide occupies a somewhat special position since it is not a source of hydrogen ions. It is known, however, that amides are capable of combining with carbon dioxide to form salts of substituted carbamic acids. Frenkel and Katchalski [12] showed that esters of α-amino acids form with CO_2 salts of N-carboxy- α-amino acids:

$$2R-CH(NH_2)COOR' + CO_2 \rightleftharpoons R-\underset{\underset{COOR'}{|}}{CH}NHCOONH_2\underset{\underset{COOR'}{|}}{CH}-R .$$

It may be suggested that these salts, like salts of all other acidic catalysts, are formed when the catalysts are added to esters of amino acids and are catalysts of the process of polycondensation of esters of α-amino acids. Here we must point out that amino acids themselves, as we proved in the case of D, L-alanine, do not possess catalytic properties; this is probably bound up with the circumstance that the carboxyl group of amino acids, as is now

assumed [11], is linked with the amino group in the form of an inner salt (betaine form).

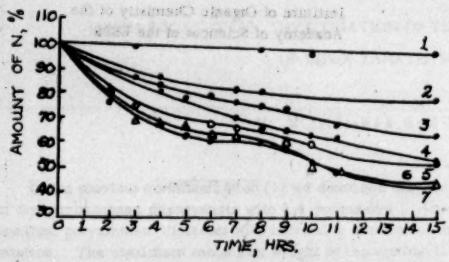

Fig. 4 Dependence of amount of nitrogen evolved in the Van Slyke analysis on the duration of the polycondensation of the ethyl ester of D,L-alanine; at 55°: 1) without catalyst; 2) in presence of 0.5% CO_2; 3) in presence of 1% CO_2; 4) in presence of 1.5% CO_2; 5) in presence of 3% acetic acid; 6) in presence of 2% CO_2; 7) in presence of 3% CO_2.

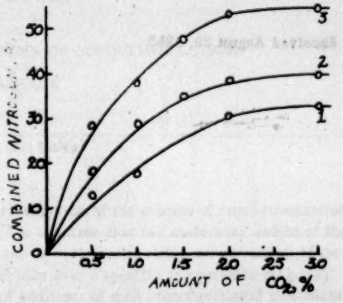

Fig. 5. Dependence of amount of combined amino nitrogen on the amount of added CO_2 in percentages of weight of ethyl ester of D,L-alanine: 1) for a reaction duration of 4 hours; 2) 8 hours; 3) 15 hours.

SUMMARY

1. The effect of various substances on the polycondensation of the ethyl ester of D,L-alanine was investigated.

2. Acids including carbonic acid in the form of carbon dioxide were found to sharply accelerate the polycondensation of esters of α-amino acids, whereas bases and amino acids are inactive.

3. The kinetics of polycondensation of the ethyl ester of D, L-alanine in presence of CO_2 and acetic acid and in the absence of catalysts was investigated.

4. It was established that with falling temperature the amount of cyclic dimer decreases and that of linear polymer increases in the polycondensation of the ethyl ester of D,L-alanine.

5. Co-polycondensation of ethyl esters of D,L-phenylalanine and glycine is shown to lead to formation of water-soluble products.

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Received August 29, 1953

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HIGH MOLECULAR COMPOUNDS

COMMUNICATION 66. INVESTIGATION OF THE KINETICS OF COPOLYMERIZATION OF DIISOCYANATES WITH GLYCOLS

V. V. Korshak and I. A. Gribova

In the previous communication [1] we described the results of investigation of the process of copolymerization of diphenylmethane diisocyanate with 1,4-butanediol. It was found at the time that the molecular weight of the resultant polyurethan increases with increasing duration of the reaction as well as with rising concentration of the solution. The maximum molecular weight of the urethan is reached only over a specific temperature range [2]. The influence was investigated of excess of starting substances and of additions of such monofunctional substances as monohydric alcohols and amines, and it was shown that with increasing amount of additives the molecular weight of the resultant polyurethane decreases. It was established that polyurethans, like all heterochain polymers, are destroyed on heating with alcohols, carboxylic acid amides or isocyanates due to alcoholysis, aminolysis, acidolysis or isocyanolysis. It was suggested that these reactions may in certain conditions also play an important part in the process of synthesis of polyurethans [1, 2].

In this paper we present the results of investigations carried out on the kinetics of copolymerization of diphenylmethane diisocyanate with 1,4-butanediol in nitrobenzene solution.

EXPERIMENTAL

Experimental procedure. The kinetics of the reaction of diphenylmethane diisocyanate with 1,4-butanediol was studied at two concentrations: 0.0703 and 0.352 mole/l. A different procedure was applied for each concentration. In experiments in which the concentration of the starting substances was 0.0703 mole/l, we used our previously described procedure[1]. The solution of the starting substances in nitrobenzene were heated in a thermostat at the experimental temperature, in the present instance 145°, and from the solution at definite time intervals were pipetted-off 10 ml samples of the reaction mass. The samples were placed in a small flask with a ground glass stopper and cooled in snow to stop the reaction.. Three 2 ml portions of the cooled reaction mass were then pipetted off. The content of free isocyanate groups was determined by titration with a chlorobenzene solution of dipropylamine by the method described below.

In experiments carried out with a concentration of starting substances of 0.352 mole/l the high viscosity of the reaction solution made it difficult to withdraw samples, and it was therefore necessary to conduct the reaction in ampoules. Weighed quantities of diphenylmethane diisocyanate and 1,4-butanediol and the requisite amount of nitrobenzene were placed in a flask with a ground-glass stopper and heated to 50° (at lower temperatures the 1,4-butanediol does not dissolve in nitrobenzene). After the 1,4-butanediol had dissolved, the hot solution was run into a series of 5 ml ampoules which were then sealed and placed in a thermostat heated to the required temperature, in this case 145 or 155°. At definite time intervals two ampoules were removed from the thermostat, quickly cooled in snow and opened; the contents of each ampoule were poured into separate flasks with ground-glass stoppers. Each ampoule was rinsed out with 10 ml nitrobenzene which was then added to the flask. The solution in the flask was titrated with a chlorobenzene solution of dipropylamine for determination of isocyanate groups by the method described below.

Determination of isocyanate groups. Into the flask containing the solution for analysis was run 5 ml 10% solution of dipropylamine in chlorobenzene. The mixture was stood on ice for 30 minutes. To the flask was then added 25 ml ethyl alcohol and 15 ml 0.5 N alcoholic NaOH in presence of a mixture of indicators (10 drops methylene blue and 5 drops methylene red). A blank determination was performed at the same time of the dipropylamine content of the chlorobenzene solution. The blank was titrated in the same manner as described above.

Determination of molecular weights of polyurethans from the content of terminal isocyanate groups. The sample of polyurethan to be analyzed for terminal isocyanate groups is subjected to the following preliminary treatment

for the purpose of keeping intact the isocyanate groups at the end of the chain and at the same time eliminating impurities. The hot reaction mass is poured from the flask into ten times the volume of dry acetone and the resultant precipitate is quickly filtered and dried in a vacuum-desiccator over phosphorus pentoxide. The dry powder is quickly pulverized in a mortar and sifted through a thick screen. A weighed amount of 1-2 g of the so-prepared polyurethan is placed in a flask with a ground-glass stopper to which are then added 3 ml of a 10% solution of piperidine in chlorobenzene and 10 ml chlorobenzene to ensure that the sample of polymer is completely covered with a layer of liquid. The flask is placed in a thermostat and heated at 80° for 30 minutes. The flask was then withdrawn and cooled in ice. The unreacted piperidine is back-titrated with 0,1 N alcoholic HCl in presence of 10 drops methylene blue and 5 drops methylene red. At the same time a blank titration is performed on the original solution of piperidine in chlorobenzene. The difference between the number of milliliters of 0,1 N HCl consumed in titration of the piperidine in the blank and in the presence of polyurethan corresponds to the number of isocyanate groups. The calculation of the molecular weight of products obtained with use of excess of diisocyanate made allowance for the presence of isocyanate groups at both ends of the molecule [3], using the formula:

$$M = \frac{20\,000 \cdot a}{b \cdot k},$$

where M is the molecular weight of the polyurethane; a is the weight of the polyurethan sample, in g; b is the consumption of 0,1 N HCl in milliliters; 20,000 is the number of milliliters of 0,1 N HCl required for one mole of polyurethan.; K = correction liter for HCl. In Table 1 are set forth examples of determination of molecular weight of polyurethans on the basis of the number of terminal isocyanate groups and of the viscosity.

TABLE 1

Comparison of molecular weights of polyurethans as determined from the number of terminal isocyanate groups and from the viscosity

Excess of diisocyanate in mole-%	Mol. wt. from no. of end groups	Viscosity of 0,5% solution in phenol (80°)	Mol. wt. determined from the viscosity
11,0	11 580	0,2063	12 720
11,0	12 380	0,2063	12 720
18,4	11 480	0,1991	12 330

Results obtained. Results of experiments with concentration of 0,0703 mole/l of the starting solution at 145° are set forth in Table 2.

Experiments with a concentration of 0,352 mole/l were performed by the other method due to the high viscosity of the solution, as mentioned above, at temperatures of 145 and 155°. The results are set forth in Tables 3 and 4.

TABLE 2

Kinetics of the reaction of diphenylmethane diisocyanate with 1,4-butanediol at 145° and conc. of 0.0703 mole/l

Duration in min.	Degree of completeness of reaction p	Extent of reaction c_p	x in mole-%	(a − x) mole-%	$\frac{x}{(a-x)\,a}$	K in l/mole min.
10	0,295	1,41	0,0221	0,0482	6,54	0,651
20	0,355	1,55	0,0261	0,0442	8,42	0,421
30	0,417	1,71	0,0304	0,0399	10,83	0,361
60	0,523	2,10	0,0376	0,0327	16,38	0,273
120	0,706	3,40	0,0502	0,0201	35,48	0,295
180	0,797	4,90	0,0564	0,0139	59,18	0,328

In addition to determination of the amount of starting materials after various intervals of time, which gave the reaction velocity as a function of the reaction temperature and the concentration of starting substances, we determined the molecular weight of the polyurethans formed. The results are set forth in Table 5, in which for comparison is included the degree of completeness of the reaction at various intervals of time.

Evaluation of results obtained. The results of our investigation of the reaction of diphenylmethane diisocyanate with 1,4-butanediol, set forth in Tables 2 to 5, permit us to draw a series of important conclusions about the kinetics of the reaction of diisocyanates with glycols and about the mechanism of this reaction. We shall first consider the influence of the concentration of the starting substances.

TABLE 3

Kinetics of reaction of diphenylmethane diisocyanate with 1,4-butanediol at 145° and a conc. of 0,352 mole/l

Duration in min.	Degree of completeness of reaction p	Extent of reaction c_p	x in mole/l	(a − x) mole/l	$\frac{x}{(a-x)\,a}$	K in l/mole min.
10	0,826	5,6	0,2958	0,0564	14,88	1,488
20	0,870	7,6	0,3066	0,0457	23,95	1,150
30	0,872	7,8	0,3151	0,0372	24,02	0,800
60	0,938	16,1	0,3305	0,0218	43,07	0,720
120	0,965	28,5	0,0340	0,0122	78,86	0,650
300	0,965	28,5	0,0340	0,0122	78,86	0,650

TABLE 4

Kinetics of reaction of diphenylmethane diisocyanate with 1,4-butanediol at 155° and conc. of 0,352 mole/l

Duration in min.	Degree of completeness of reaction p	Extent of reaction c_p	x in mole/l	(a − x) mole/l	$\frac{x}{(a-x)\,a}$	K in l/mole min.
10	0,827	5,7	0,2931	0,0607	13,363	1,363
20	0,882	8,4	0,3123	0,0415	21,3	1,06
30	0,923	12,9	0,3267	0,0271	34,0	1,13
60	0,956	22,7	0,3382	0,0155	61,4	1,02
120	0,976	41,7	0,3459	0,0079	123,4	1,03
300	0,995	–	–	–	–	–

TABLE 5

Change of molecular weight of polyurethans in dependence on the reaction temperature at a conc. of 0,352 mole/l

Duration in min.	Reaction temperature					
	145°			155°		
	Degree of completeness of reaction p	Viscosity of 0,5% solution in aq. phenol	Mol. wt. of polyurethan	Degree of completeness of reaction p	Viscosity of 0,5% solution in aq. phenol	Mol. wt. of polyurethan
10	0,826	–	–	0,827	–	–
20	0,870	–	–	0,882	–	–
30	0,872	0,082	5 000	0,923	0,105	6 500
60	0,938	0,109	6 700	0,956	0,134	8 300
90	–	0,132	8 200	–	0,153	9 500
120	0,965	–	–	0,976	–	–
180	–	0,167	10 300	–	0,212	13 200
300	0,965	0,203	12 600	0,995	0,244	15 200

As we see from Fig. 1, with rise of concentration of the initial reactants (at the same temperature of 145°) there is a considerable increase in reaction velocity which enables a degree of completeness of the reaction of 0,826 to be reached at a concentration of 0,352 mole/l in 10 min, whereas at a concentration of 0,0703 mole/l this degree of completeness requires 180 minutes.

Fig. 2 illustrates the change of extent of reaction (c_p) as a function of the concentration and reaction of temperature.

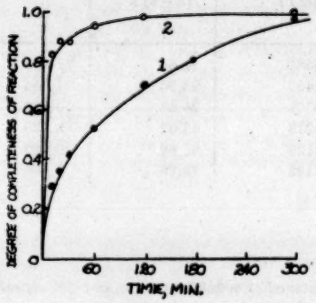


Fig. 1 Kinetics of copolymerization of diphenylmethane diisocyanate with 1,4-butanediol at 145°. 1) Conc. of starting substances 0.0703 mole/l; 2) conc. of starting substances 0.352 mole/l.

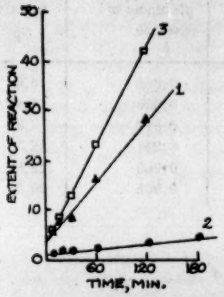


Fig. 2. Change of extent of reaction of copolymerization of diphenylmethane diisocyanate with 1,4-butanediol at various concentrations and temperatures: 1) 145°, 0.3523 mole/l; 2) 145°, 0.07028 mole/l; 3) 155° 0.3538 mole/l.

It is clear from the graph that the extent of reaction, denoting the ratio of the initial number of functional groups introduced into the reaction to the number of functional groups at the given instant ($c_p = N_0/N$), also increases with the concentration and temperature of the reaction.

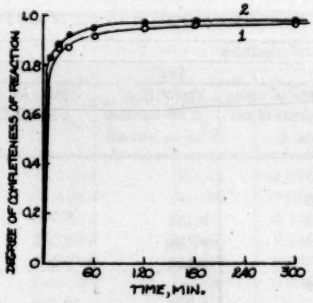


Fig. 3. Dependence of degree of completeness of the reaction on the duration of the experiment: 1) at 145°; 2) at 155°.

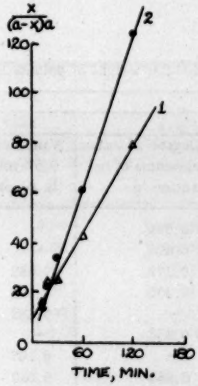


Fig. 4. Graphical determination of velocity constants at a conc. of starting substances of 0.253 mole/l: 1) At 145°; 2) at 155°.

The influence of the reaction temperature at a concentration of the initial substances of 0.352 mole/l is shown in Fig. 3.

We see from Fig. 3 that a 10° rise of temperature (from 145 to 155°) leads to appreciable acceleration of the reaction.

We determined the order of the reaction (van't Hoff) (see Tables 2,3, and 4) and found that the reaction of diphenylmethane diisocyanate with 1,4-butanediol is of the second order as a bimolecular reaction. The mean value of the velocity constants was determined from the tangent of the angle of slope of the straight line obtained by plotting (ordinates) the value of $\frac{x}{(a-x)a}$, against (abscissas) time. The mean value of the constants at 145° was found to be 0.571 liters/(moles · min.), while at 155° the value was unity. The graphs from which the mean values of the constants were determined are plotted in Fig. 4.

The data obtained were used to calculate the temperature coefficient of the reaction; for the range 145-155° it was found to be 1.751. The activation energy of the reaction of diphenylmethane diisocyanate with 1,4-butanediol was found to be 19,900 cal/mol.

The data of Table 5 were applied to the construction of the curves shown in Fig. 5; these show the change in molecular weight of the formed polyurethan during the reaction and the simultaneous change in the degree of completeness of reactions, i.e. the rate of consumption of the starting substances.

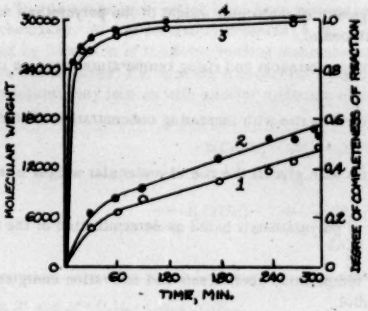


Fig. 5. Dependence of molecular weight 1) At 145°; 2) at 155°) and degree of completeness of reaction 3) at 145°; 4) at 155°) on the duration of an experiment.

Inspection of these curves enables us to draw some extremely important conclusions regarding the growth of the polyurethan molecule during the reaction. On comparing curves 1 and 2 (relating to 145°) with curves 3 and 4 (relating to 155°), it is easy to see that there is no complete correlation between the degree of completeness of the reaction and the rise of molecular weight of the polyurethan. After a period of only 60 minutes, 94-96% of the starting substances has been consumed but the molecular weight in spite of this continues to rise twice as much in the following 240 minutes although the change in the amount of starting materials over this period is only 2.5-3.5%. Consequently the growth of the polyurethan molecule during the latter stages of the reaction does not involve molecules of the initial monomers but is the result of interaction between the macromolecules.

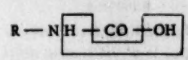
This conclusion is fully consistent with the results of investigation of the polycondensation of 1,6-hexanediol with sebacic acid which one of us carried out in collaboration with Vinogradova [4]. This investigation also revealed that the starting monomers disappear in the very first stages of the reaction, notwithstanding which the growth of molecules of the polyester continues subsequently by interaction of the macromolecules among themselves.

This conclusion has considerable significance for the understanding of many chemical reactions of high-molecular compounds, since it shows that macromolecules possess considerable mobility and consequently considerable reactivity. This aspect must be taken into account in all cases. Reactions between macromolecules can evidently have great importance in various processes, including polymerization.

In conclusion we shall consider briefly some characteristics of the reaction of diisocyanates with glycols. Regarding, first of all, the known analogy between reactions of diisocyanates and those of ketenes, this similarity can be understood if we take into account the fact that ketenes are inner anhydrides of carboxylic acids:

$$R - CH\boxed{H - CO - OH} \ .$$

while isocyanates can likewise be reagarded as inner anhydrides of carbamic acids:



This analogy harmonizes with the close similarity in the reactions of isocyanates and ketenes, as manifested by the fact that the most typical reactions of both classes of compounds are addition reactions at the double bonds of various substances containing mobile hydrogen atoms, such as alcohols, acids and amines, or polymerizations (which are essentially additions between like molecules). Consequently the following considerations about reactions of isocyanates are evidently applicable in equal measure to reactions of ketenes.

It may be suggested that the carbon-nitrogen double bond in isocyanates is strongly polarized under the influence of the oxygen atom and therefore tends strongly to link with polarized molecules according to the scheme:

$$R-N=\overset{\delta+}{C}=O+R^1\overset{\delta-}{O}-\overset{\delta+}{H}\rightarrow R-NH-COO-R^1.$$

This accounts for the fact that the reaction of isocyanates with glycols and, in particular, with the more strongly polarized amines, proceeds extremely rapidly with a velocity typical of ionic reactions.

SUMMARY

1. The kinetics of the reaction of copolymerization of diphenylmethane diisocyanate with 1,4-butanediol was investigated at 145 and 155° in nitrobenzene solution at concentrations of 0.352 and 0.0703 mole/l.

2. A study was made of the dependence on time of the growth of molecular weight of the polyurethan during copolymerization of diphenylmethane diisocyanate and 1,4-butanediol.

3. It was found that increasing concentration of the starting substances and rising temperature speed up the copolymerization of diisocyanates with glycols.

4. The molecular weight of the polyurethan formed is found to rise with increasing concentration of starting substances and rising temperature.

5. In the later stages of copolymerization of diisocyanates with glycols the rise of molecular weight is mainly due to mutual interaction of the pdyurethan macromolecules.

6. A new method of determination of molecular weight of polyurethans is based on determination of the terminal isocyanate groups.

7. Determinations were made of the velocity constants, temperature coefficients and activation energies of the reaction of diphenylmethane diisocyanate with 1,4-butanediol.

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Received August 29, 1953

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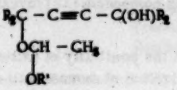
**" " " " , p. 967.

INVESTIGATION OF ACETYLENIC ALCOHOLS AND GLYCOLS

COMMUNICATION 3. STEPWISE SYNTHESIS OF ACETALS OF ACETYLENIC GLYCOLS

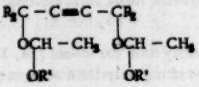
M. F. Shostakovsky and A. V. Bogdanova

The synthesis and investigation of the properties of acetylenic glycols are of undoubted interest in view of their great reactivity. In previous communications [1, 2] methods were presented for synthesis of mono- and dialkyl acetals of acetylenic alcohols with the general formulas:



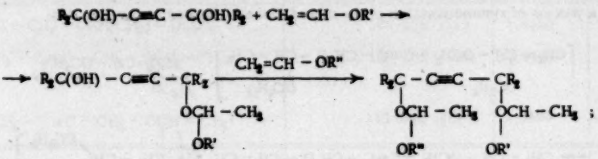
(I)

and



(II)

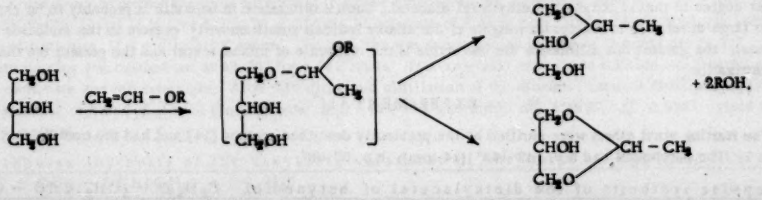
The new substances which have been synthesized and the methods for their synthesis are of interest for acetylene chemistry. As was previously observed [1, 2], the synthesis of diacetals of acetylenic glycols is always accompanied by formation of the corresponding monosubstituted acetals. For this reason we suggested that a stepwise reaction was involved, i.e. that the monoacetal formed in the first step may either be isolated or (if left in the reaction medium) may join on with another molecule of vinyl ether to form the diacetal in accordance with the following equations:



where R' and R" = C_2H_5; C_4H_9; C_8H_{17}.

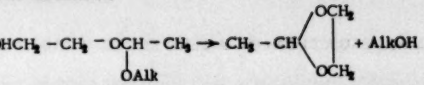
The stepwise mechanism of the synthesis enables two series of derivatives of acetylenic glycols to be obtained: mono- and diacetals. Most of the known derivatives of acetylenic glycols are disubstituted compounds [3, 4]. Monosubstituted acetylenic derivatives reported in the literature are the partial ethyl and isoamyl ethers of tetramethylbutynediol which were prepared and examined by Zalkind [5]. It is interesting that the formation of monoacetals of the type of (I), as well as of mixed acetals, is only found possible for the acetylenic glycols series. In the case of saturated or of olefinic glycols, as well as of glycerol and other polyhydric alcohols, attempts to separate the mono- and diacetals have proved unsuccessful due to cyclization [6, 7, 8, 9].

In the case of glycerol [8] this process takes place according to the scheme:



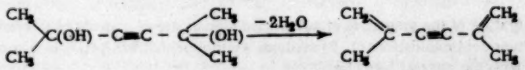
Reaction of ethyleneglycol with vinyl ethers usually leads to dicyclic acetals [9], and only the application of exceptional synthesis conditions (excess of vinyl ether, a strict temperature limit and absence of acid catalyst) enabled this author to partly avoid cyclization. The isolated ethylene glycol monoacetals, however, proved to be very

unstable and underwent cyclization on distillation:



Dehydration of tetramethyl- and tetraphenylbutynediols [10, 11] was observed on their condensation with phenol; during this process the phenol added on to the triple bond of the glycol.

The literature also contains earlier reports of the hindering effect of the triple bond, for example during dehydration of acetylenic glycols [12]. In this case, instead of the cyclization which occurs with saturated pinacones, formation takes place of unsaturated hydrocarbons:

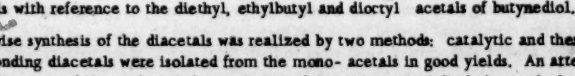


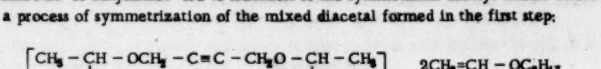
Similarly a study of the magnetic fields of acetylenic hydroxyl-containing compounds [13] revealed the screening effect of the triple bond.

Investigations by Favorsky and his school [14, 15, 16] demonstrated the possibility of existence of carbocyclic systems with a triple bond, starting only from an 8-membered ring. Cyclization of monoacetals of acetylenic glycols is also excluded by the circumstance that the triple bond creates a great strain in the hydrocarbon chain of the molecule, hindering the cyclization which might have led to formation of only a 7-membered ring.

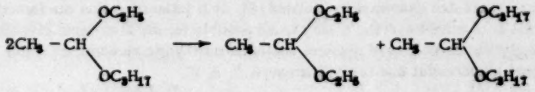
In this communication experimental confirmation is given of the stepwise formation of diacetals of acetylenic glycols with reference to the diethyl, ethylbutyl and dioctyl acetals of butynediol.

Stepwise synthesis of the diacetals was realized by two methods: catalytic and thermal. By these methods the corresponding diacetals were isolated from the mono- acetals in good yields. An attempt to obtain the mixed ethyloctyl diacetal of butynediol led to isolation of the symmetrical diethyl acetal whose formation may be explained by a process of symmetrization of the mixed diacetal formed in the first step:





Symmetrization of the mixed ethyloctyl acetal of acetaldehyde gives, in accordance with the following scheme, the acetaldehyde dioctyl acetal which we isolated:



It is interesting that symmetrization was observed mainly in the case of butynediol ethyloctyl diacetal and to a lesser degree in that of butynediol ethylbutyl diacetal. Such a difference in behavior is probably to be explained by the large difference in molecular weights of the alkoxy radicals simultaneously present in the molecule of the diacetal: the greater this difference the less stable is the molecule of mixed acetal and the greater the tendency to symmetrization.

EXPERIMENTAL *

The starting vinyl ethers were purified by the previously described method [14] and had the constants set forth in Table 1. The butynediol had b.p. 142-143° (14 mm); b.p. 57-58°.

I. Stepwise synthesis of the diethylacetal of butynediol $C_2H_5O-(CH_3)CHO-CH_2-C\equiv C-CH_2-OCH(CH_3)-OC_2H_5$.

Preparation of butynediol monoethylacetal by the thermal method. Heating in an autoclave to 81-88° of a

* Senior laboratory technician M. S. Egorova participated in the experimental work.

mixture of 43 g (0.5 mole) butynediol and 37 g (0,5 mole) vinylethyl ether for 2 hours followed by vacuum distillation gave 60.2 g (77,0% of the theoretical) of the monoethyl acetal of butynediol with constants (Table 2) in accordance with the literature [1].

TABLE 1

Constants of initial vinyl ethers

No.	Ether	B.p. in °C (p in mm Hg)	n_D^{20}
1	Vinylethyl	36,0-36,5	1,3785
2	Vinylbutyl	93,0-93,5	1,4035
3	Vinyloctyl	59-60 (10 mm)	1,4275

Preparation of butynediol diethylacetal from the monoacetal by the thermal method. Into a stainless steel bomb of 300 ml capacity were charged 33,5 g butynediol monoethylacetal and 17,0 g vinylethyl ether. The bomb was heated on an oil bath to 100-105° for 12 hours. 49,6 g light-yellow product was discharged and on vacuum fractionation gave the following fractions:

Fraction I, B. p. to 137° (33-18 mm); 8,2 g
Fraction II, B. p. 137-138° (18 mm); 35,3 g
Residue 4,9 g

Fraction I contained unreacted vinylethyl ether with b.p. 36,0-36,5° and n_D^{20} 1,3775.

Fraction II was the diethylacetal of butynediol with constants (Table 2) agreeing with the literature [1]. Its yield was 72,4 % of the theoretical.

TABLE 2

Constants of the prepared acetals

No.	Formula of acetal	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
1	$HO-CH_2-C\equiv C-CH_2-OCH(CH_3)-OC_2H_5$	127-128 (11)	1,4550	1,0188
2	$CH_3-CH(OC_2H_5)-CH_2-C\equiv C-CH_2-OCH(OC_2H_5)-CH_3$	137-138 (18)	1,4400	0,9743
3	$CH_3-CH(OC_2H_5)-CH_2-C\equiv C-CH_2-OCH(OC_4H_9)-CH_3$	141-142 (6)	1,4420	0,9595
4	$CH_3-CH(OC_8H_{17})_2$	150-151,5 (7)	1,4315	0,8408
5	$CH_3-CH(OC_8H_{17})-CH_2-C\equiv C-CH_2-OCH(OC_8H_{17})-CH_3$	161-165 (0,05)	1,4500	0,9150

Preparation of diethylacetal of butynediol from the monoacetal by a catalytic method. To a solution of 20 g monoethylacetal of butynediol in 20 g dioxane in presence of 3 drops conc. hydrochloric acid was added dropwise, with stirring, 11,0 g vinylethyl ether. The addition was accompanied by rise of temperature to 30°. The subsequent heating was carried out at 48-50° for 4 1/2 hours. The outwardly unchanged solution was treated with potassium carbonate and left overnight. After filtration and distillation of the dioxan, vacuum distillation gave 28,7 g diethylacetal of butynediol with the constants: b.p. 140-141° (20 mm); n_D^{20} 1,4395; d_4^{20} 0,9727; yield 98,3% of the theoretical.

II. Stepwise snythesis of the ethylbutyl diacetal of butyneiol [$C_2H_5O(CH_3)CHO-CH_2-C\equiv C-CH_2-OCH(CH_3)-OC_4H_9$]

Preparation of butynediol monoethylacetal. The preparation was described above.

Preparation of ethylbutylacetal of butynediol from the monoethylacetal by the catalytic method. To a

solution of 15.0 g butynediol monoethylacetal in 10 g dioxan in presence of a drop of conc. hydrochloric acid at room temperature was added 12.0 g vinylbutyl ether. The mixture was then heated for 3 hours at 40°; the dioxan was driven off and the residue fractionated in vacuum:

Fraction I	B. p. 130-154° (13 mm);	9.7 g
Fraction II	B. p. 154-162° (13 mm);	6.5 g
Residue		7.5 g

From Fraction I was recovered 3 g unchanged butynediol monoethylacetal with the constants: b.p. 130-131° (14 mm); n_D^{20} 1.4550; d_4^{20} 1.0185.

From Fraction II was separated 4.5 g of a product with the constants: b.p. 141-142° (6 mm); n_D^{20} 1.4420; d_4^{20} 0.9595; found MR 71.23; calculated MR 71.36

	Found %:	C 64.45; 64.38; H 9.91; 9.98
$C_{14}H_{26}O_4$.	Calculated %:	C 64.83; H 10.09
	Found M:	238.90
$C_{14}H_{26}O_4$	Calculated M:	258.35

Hydrolysis and acetal determination (methods described in [1, 2]): 97.2; 98.0%.

The constants and analysis of the isolated product identify it as butynediol ethylbutyl diacetal. Its yield is 28.1% of the theoretical. Butynediol ethylbutyl diacetal was also prepared by the thermal method, by heating equimolar amounts of butynediol monoethyl acetal and vinylbutyl ether at 115-120° for 12 hours in a bomb.

III. Reaction of butynediol monoethyl acetal with vinyloctyl ether

$[C_2H_5O(CH_3)CHO-CH_2-C\equiv C-CH_2OCH(CH_3)-OC_8H_{17}]$

The starting material for this synthesis was the above-described butynediol monoethyl acetal. To a solution of 25.3 g butynediol monoethyl acetal in 23 g dioxan in presence of 3 drops conc. HCl was added dropwise at 60-65° 26 g vinyloctyl ether. The mixture was then heated to 80-85° for 16 hours; the dioxane was driven off and the residue fractionated in low vacuum:

Fraction I	B. p. 122-155° (6 mm),	30.0 g
Fraction II	B. p. 155-185° (10 mm),	13.4 g
Residue		7.0 g

Refractionation of Fraction I gave 7.5 g of a product with the following constants: b.p. 150-151.5° (7 mm); n_D^{20} 1.4315; d_4^{20} 0.8408; found MR 88.29; calculated MR 88.61.

	Found %:	C 74.84; 74.93; H 13.20; 13.32
$C_{18}H_{38}O_2$.	Calculated %:	C 75.46; H 13.37
	Found M:	268.1; 274.1
$C_{18}H_{38}O_2$	Calculated M:	286.48

The constants and analysis of the isolated product identify it as acetaldehyde dioctyl acetal [17]. Yield 15.7% of the theoretical.

From Fraction II was isolated 10 g of product with the constants: b.p. 161-165° (0.05 mm); n_D^{20} 1.4500; d_4^{20} 0.9150; found MR 116.9; calculated MR 117.10. (Even in high vacuum the product distils with slight decomposition.)

	Found %:	C 71.81; 71.67; H 11.54; 11.38
$C_{34}H_{66}O_4$.	Calculated %:	C 72.31; H 11.63
	Found M:	349.30; 336.50
$C_{34}H_{66}O_4$.	Calculated M:	338.61

Hydrolysis and acetal determination: 97.57; 96.62%.

The constants found and the analysis enable us to regard the isolated product as butynediol dioctyl acetal. Yield 15.1% of the theoretical.

SUMMARY

1. The stepwise mechanism of the addition of vinyl ethers to acetylenic glycols was confirmed.

2. The intermediate products of this reaction – monoacetals of acetylenic glycols – were isolated in good yields both by thermal and by catalytic methods.

3. The following corresponding diacetals were prepared from the monoacetals of acetylenic glycols by various methods: diethyl, ethylbutyl and dioctyl; the two latter were prepared for the first time.

4. It was demonstrated that in the preparation of mixed diacetals from the corresponding monoacetals, the main reaction is accompanied by a process of symmetrization which is intensified with increasing difference between the molecular weights of the radicals of the starting vinyl ethers. The result of this process is the formation of a symmetrical diacetal consisting of the product of substitution of the low-molecular alkoxy group by the higher molecular one.

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Received September 21, 1953

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INVESTIGATIONS OF THE INTERACTION BETWEEN VINYL AND POLYFUNCTIONAL COMPOUNDS

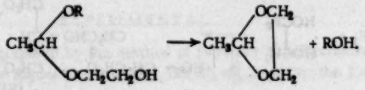
COMMUNICATION 3. REACTION OF GLYCEROL TRIVINYL ETHER WITH ETHYLENE GLYCOL AND 1,4-BUTANEDIOL

M. F. Shostakovsky, V. V. Zhebrovsky and M. A. Medelyanovskaya

In previous communications on the reaction of vinyl ethers with glycerol [1] and with polyvinyl alcohol [2] it was established that the reaction always proceeds with formation of the corresponding cyclic acetals.

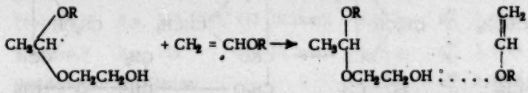
The present investigation is devoted to a study of the course of the reaction in the case when both components are polyfunctional compounds, using glycerol trivinyl ether and glycols (ethylene glycol and 1,4-butanediol) as models. It has been shown [3] that in many reactions the interaction of the hydroxyl groups of ethylene glycol proceeds either stepwise or simultaneously, thus necessitiating the selection of appropriate conditions for preparing its mono- and difunctional derivatives.

In the interaction of ethylene glycol with alkylvinyl ethers the formation of monoalkyl acetals is observed on heating, whereas the corresponding dialkyl acetals of ethylene glycol are predominantly formed in presence of a catalyst. At the same time the monoactals are found to be easily transformed into cyclic acetals:



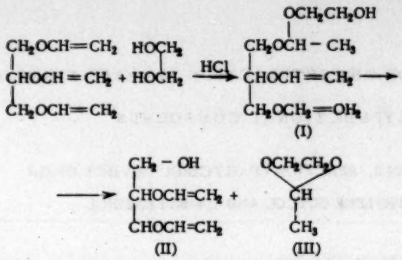
The ratio of starting components is of great importance. Thus, molar ratios (1:1) of vinyl ether and ethylene glycol lead to monoalkyl acetals, whereas with equivalent (2:3) amounts of reactants the corresponding cyclic acetal is formed.

Dialkyl acetals of ethylene glycol are obtained by reacting the latter with excess of the vinylalkyl ether in presence of a catalyst. The excess of the vinyl ether is an important factor since the reversal of the order of addition of the reactants leads to the reaction being shifted in the direction of cyclization of the monoacetal. The authors believe that this is due to the fact that acetalization of one hydroxyl group of ethylene glycol enhances the activity of the hydrogen of the remaining hydroxyl group, leading to cyclization of the monoacetal with separation of the alcohol. In presence of an excess of vinyl ether, however, the transformation of the monoacetal into a cyclic acetal is hindered by formation of a hydrogen bond.



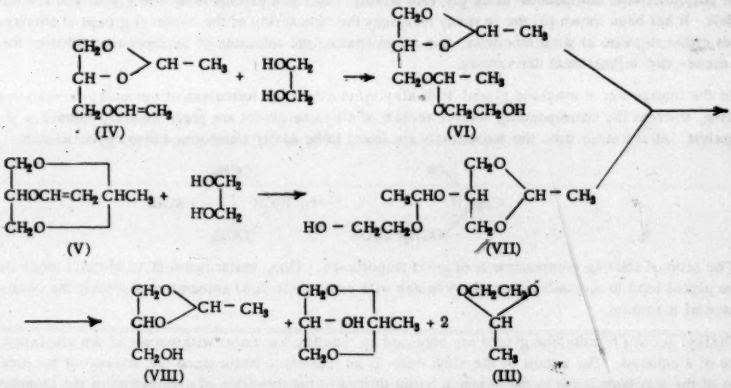
Formation of acetals of glycols containing free hydroxyl groups was observed in the case of unsaturated glycols. In the latter the factor hindering cyclization is the presence of a triple bond. In an investigation of the reaction of vinyl ethers with tetramethylbutynediol and 1,4-butynediol, one of us in collaboration with Bogdanova [4, 5] did not isolate the cyclic acetals; the reaction yielded the mono- and diacetals of tetramethylbutynediol and 1,4-butynediol, and it was observed that the formation of diacetals proceeds through the stage of formation of monoacetals whose yield depends on the synthesis conditions.

In the present investigation of the reaction of glycerol trivinyl ether with ethylene glycol and 1,4-butanediol, it was found that the inevitable product of the first stage of reaction of glycerol trivinyl ether with ethylene glycol in molar ratios was the mixed acetal of glycerol vinyl ether and ethylene glycol (I).

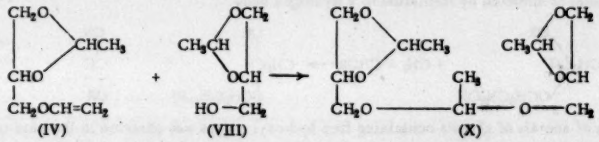


which, being unstable, breaks down to the partial vinyl ether of glycerol (II) and the cyclic acetal of ethylene glycol (III).

Isomerization of the divinyl ether of glycerol (II) leads to formation of the 1,2- and 1,3-acetals of the monovinyl ether of glycerol (IV) and (V). The latter react with ethylene glycol to form the mixed acetals (VI) and (VII) which break down to 1,2- and 1,3-acetals of glycerol (VIII) and (IX) and the acetal of ethylene glycol (III):



The isomeric acetals (VIII) and (IX) are separated by taking advantage of the different solubilities of their benzoates in low-boiling gasolines. The triacetal of glycerol was also isolated during the investigation; its formation could result from interaction of acetals (IV) and (VIII):

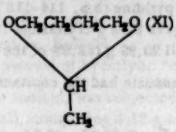


With equimolar ratios of glycerol trivinyl ether and ethylene glycol (2:3) the reaction mainly proceeds with formation of the cyclic acetals of glycerol and ethylene glycol (III) and (VIII).

The formation of a minor amount of glycerol 1,3- acetal (IX) may be explained in the following manner: reaction of glycerol trivinyl ether with ethylene glycol gives in the first instance a mixed acetal involving the α-vinyl group of the ether; this mixed acetal evidently then breaks down to the 1,2-divinyl ether of glycerol which isomerizes to the monovinyl ether of glycerol 1,2-acetal owing to the spatial closeness of the free primary OH group to the vinyl group in the α-position.

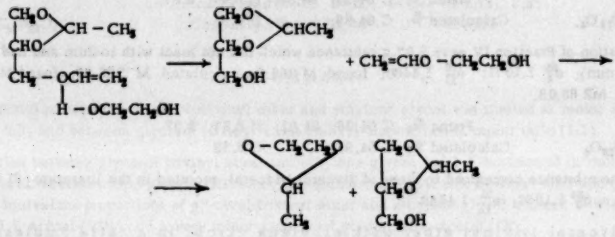
In the interaction of glycerol trivinyl ether with 1,4-butanediol, using molar ratio of components, cyclic acetals are evidently formed according to the same scheme as for ethylene glycol. We actually isolated

the cyclic acetal of 1,4-butanediol:



the two glyceryl acetals (VIII) and (IX) and the glyceryl triacetal (X).

Formation of cyclic acetals of ethylene glycol and 1,4-butanediol can be explained by the following mechanism: After establishment of a hydrogen bond between the oxygen of the 1,2-glyceryl acetal and the hydrogen of ethylene glycol or 1,4-butanediol vinyl rearrangement proceeds according to the scheme:



Consequently the formation of cyclic acetals of ethylene glycol and 1,4-butanediol is accompanied by indirect vinylation of the latter.

EXPERIMENTAL

The glycerol trivinyl ether was prepared by the method of Favorsky and Shostakovsky and had b.p. 164-165°; n_D^{20} 1.4382; d_4^{20} 1.03325; the ethylene glycol had b.p. 196-196.5°; n_D^{20} 1.4279; the 1,4-butanediol had b.p. 117-118° (7-8 mm); n_D^{20} 1.4470.

Reaction of glycerol trivinyl ether with ethylene glycol in molar ratio.

42.5 g (0.25 mole) glycerol trivinyl ether and 15.5 g (0.25 mole) ethylene glycol were mixed for 1/2 hour; the catalyst consisting of 2 drops (0.028 g) hydrochloric acid was then introduced; the reaction took place instantaneously with rise of temperature to 92°. After neutralization with potassium carbonate the product was distilled from a Favorsky flask, the following fractions being obtained from the 51.88 g material in the flask:

Fraction I	B.p. 70-80°		1.45 g;		
Fraction II	B.p. 81-83°		18.08 g;	n_D^{20}	1.4008
Fraction III	B.p. 83-100°;	(11-12 mm);	24.97 g;	n_D^{20}	1.4452
Fraction IV	B.p. 157-166°;	(11-12 mm);	4.98 g;	n_D^{20}	1.4496
Fraction V	B.p. 170°	(11-12 mm);	0.76 g;	n_D^{20}	1.4620
Residue from distillation			1.52 g;	n_D^{20}	1.4615

a) Redistillation of Fraction II gave 6.76 g substance with b.p. 81-82°; d_4^{20} 0.9858; n_D^{20} 1.3999, corresponding to the cyclic acetal of ethylene glycol (III).

The literature data [6] are: b.p. 82.3°; d_4^{24} 0.9770; n_D^{24} 1.3945.

Found M: 87.60
Calculated M 88.10

Found MR 21.53
$C_4H_8O_2$. Calculated MR 21.76

Found %: C 54.03; 53.75; H 9.30; 9.18
$C_4H_8O_2$. Calculated %: C 54.54 H 9.09

b) Fraction III reacted with metallic sodium and methylmagnesium iodide and was subjected to benzoylation. To a mixture of 20 g Fraction III and 48 g pyridine (b.p. 114-115°) was gradually added 83.7 g benzoyl chloride (b.p. 75-76°) (10-11 mm). The reaction gave 8.42 g crystalline 1,3-ethylideneglyceryl benzoate and 11.36 g liquid 1,2-ethylideneglyceryl benzoate, in all 23.92 g (52.6% of the theoretical) [1].

Crystalline 1,3-ethylideneglyceryl benzoate had the constants: m.p. 84-85°; found M 224.1; calculated M 222.23.

	Found %:	C 65.03;	65.26;	H 6.31;	6.25
$C_{12}H_{14}O_4$	Calculated %:	C 64.86;		H 6.31	

1,2-Ethylideneglyceryl benzoate had the constants: b.p. 179-180° (17 mm); d_4^{20} 1.1556; n_D^{20} 1.5143; found M 220.0; calculated M 222.23; found MR 57.34; calculated for $C_{12}H_{14}O_4$ MR 57.76.

	Found %:	C 64.27;	64.35;	H 6.44;	6.37
$C_{12}O_{14}O_4$.	Calculated %:	C 64.86;		H 6.31	

c) Redistillation of Fraction IV gave 2.07 g substance which did not react with sodium and had the constants: b.p. 156-157° (11 mm); d_4^{20} 1.1071; n_D^{20} 1.4480; found M 266.7; calculated M 262.29; found MR 64.30; calculated for $C_{12}H_{22}O_6$ MR 63.08.

	Found %:	C 54.26;	54.31;	H 8.37;	8.33
$C_{12}H_{22}O_6$	Calculated %:	C 54.96;		H 8.39	

The constants of the substance correspond to those of glycerol triacetal, reported in the literature [6] to have: b.p. 160-162° (14 mm); d_4^{24} 1.1067; n_D^{20} 1.4482.

Reaction of glycerol trivinyl ether with ethylene glycol in a ratio (moles) of 2:3.

34 g glycerol trivinyl ether and 18.6 g ethylene glycol were stirred together for 1/2 hour; after introduction of 1 drop (0.014 g) hydrochloric acid, the temperature rose to 91°. Fractionation of the reaction product, after neutralization with potassium carbonate, gave:

Fraction I	B.p.	74-83.5°	(760 mm);	22.67 g
Fraction II	B.p.	80-93°	(12-14 mm);	23.38 g
Fraction III	B.p.	148-149°	(4 mm);	2.50 g
Distillation residue				2.45 g

Redistillation of Fraction I gave 15.2 g (57.6% of the theoretical) of the cyclic glycol acetal (III) with the constants: b.p. 81-82°; n_D^{20} 1.4002; d_4^{20} 0.9856.

Redistillation of Fraction II failed to yield narrower cuts. The substance (21 g) collected, with b.p. 78-90° (10 mm) and n_D^{20} 1.4430, was subjected to benzoylation. No crystallization was observed on cooling the gasoline solution of the benzoylation products. Vacuum distillation yielded 20.8 g glycerol 1,2-acetal benzoate with the constants: b.p. 165-168° (12-13 mm); n_D^{20} 1.5148; d_4^{20} 1.1569.

The residue from the distillation (4.67 g) crystallized. The crystals melted at 69-70°; after many recrystallizations from a low-boiling gasoline (60-70°), 2.6 g glycol dibenzoate with m.p. 73° [7] was obtained, together with traces of the benzoate of the 1,3-acetal of glycerol with m.p. 82-83°. Literature data: m.p. 86° [6]. Fraction III, with b.p. 148-149° (4 mm); n_D^{20} 1.4762, soluble in water and reacting with metallic sodium, was glycerol.

Reaction of glycerol trivinyl ether with 1,4-butanediol in molar ratios.

21.25 g (0.125 mole) glycerol trivinyl ether and 11.25 g (0.125 mole) 1,4-butanediol were treated in conditions similar to those of the experiment with ethylene glycol. On introducing two drops (0.028 g) of HCl the temperature rose to 99°. Fractionation of the product (29.5 g), after neutralization with potassium carbonate, gave:

Fraction I	B.p.	125-128°;	5.8 g;	n_D^{20} 1.4315
Fraction II	B.p.	77-100° (8 mm);	9.6 g;	n_D^{20} 1.4468
Fraction III	B.p.	151-156° (10 mm);	9.25 g;	n_D^{20} 1.4505
Distillation residue			3.4 g;	n_D^{20} 1.4580

a) Fraction I was the cyclic 1,4-acetal of butanediol (XI); yield 40% of theoretical; after treatment with metallic sodium and redistillation, it had the constants: b.p. 127-128°; d_4^{20} 0.9840; n_D^{20} 1.4288; found M 117.20;

calculated M 116.15; found MR 31.33; calculated for $C_6H_{12}O_2$ MR 30.99.

	Found %:	C 62.15; 62.18; H 10.55; 10.53
$C_6H_{12}O_2$.	Calculated %:	C 62.04; H 10.41

Acetal content (by method of hydrolytic "oxylation") 98.87; 99.10% [8].

b) Fraction II, which reacted with metallic sodium, was subjected to benzoylation; the yield of benzoylation products was 10.36 g (58.2% of the theoretical), comprising 4.12 g crystalline 1,3-ethylideneglyceryl benzoate with m.p. 85° and 6.24 g liquid 1,2-ethylideneglyceryl benzoate with b.p. 157-158° (10 mm); n_D^{20} 1.5143; d_4^{20} 1.1559 [6].

c) From Fraction III, after redistillation, was isolated 5.65 g substance with b.p. 154-156° (10 mm), not reacting with sodium; its constants (d_4^{20} 1.1074; n_D^{20} 1.4483) correspond to glycerol triacetal (X) [6].

	Found %:	C 54.30; 54.26; H 8.43; 8.37
$C_{12}H_{22}O_6$.	Calculated %:	C 54.96 H 8.39

SUMMARY

1. The reaction between glycerol trivinyl ether and ethylene glycol was studied at molar and equivalent ratios (1:1 and 2:3) and between glycerol trivinyl ether and 1,4-butanediol at molar ratio (1:1).

2. Reaction between glycerol trivinyl ether and ethylene glycol and 1,4-butanediol in molar ratio leads to formation of cyclic acetals of the glycols (III) and (XI), the isomeric glycerol acetals (VIII) and (IX) and glycerol triacetal (X). Equivalent proportions of glycerol trivinyl ether and ethylene glycol yielded ethylene glycol acetal (III), glycerol 1,2-acetal (VIII) and a very minor amount of glycerol 1,3-acetal (IX).

3. The formation of cyclic acetals of glycols and glycerol is accounted for by tautomerism of the corresponding acetals.

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Received May 20, 1953

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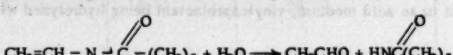
THE IONIC HYDROLYSIS OF VINYL LACTAMS IN AN ACID MEDIUM

M. F. Shostakovsky, F. P. Sidelkovskaya and M. G. Zelenskaya

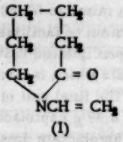
Hydration and hydrolytic cleavage constitute criteria of the reactivity of vinyl compounds. As we know, hydrolysis of a series of substances in acid and alkaline media is readily effected by an ionic mechanism. Today we know that this reaction can proceed in a neutral medium by a free-radical mechanism [1]. As was observed by Shostakovsky, a number of vinyl compounds are activated with equal ease by free-radical catalysts and by ionic catalysts. In the case of some compounds one form of activation is realized with greater facility than the other. Even in such cases, however, a suitable choice of conditions will permit reactions to be activated both by free-radical and by ionic catalysts [1].

In one of the preceding communications it was shown that vinylcaprolactam hydrolyzes under the influence of hydrogen peroxide with formation of caprolactam and acetaldehyde [2].

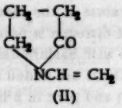


Vinyl acetate is likewise hydrolyzed under the influence of oxidizing catalysts [3]. In these cases the process takes place with a free-radical mechanism and is accompanied by polymer formation. It appeared to be of interest to investigate the ionic hydrolysis of vinyl lactams.

The present communication relates to a study of ionic hydrolysis of vinylcaprolactam (I) and vinylpyrrolidone (II) under the influence of sulfuric acid:



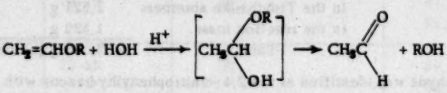
(I)



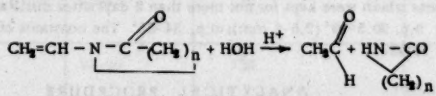
(II)

The investigated compounds were synthesized by the method of Favorsky and Shostakovsky [4].

It is known that vinylalkyl ethers with the general formula $CH_2=CHOR$ (where R is a C_1 to C_3 aliphatic radical) are readily hydrolyzed in an acid medium with formation of acetaldehyde and the corresponding alcohols. The reaction proceeds at room temperature in presence of minute amounts of acid and is extensively used for quantitative determination of vinyl ethers [5]:



In the present paper it is shown that vinyl lactams are also hydrolyzed by an ionic mechanism in presence of sulfuric acid with formation of acetaldehyde and lactams:



The process was studied in more detail with reference to vinylcaprolactam. Its hydrolysis yielded acetaldehyde and caprolactam. In working with small amounts (about 0.1 g) vinylcaprolactam, the acetaldehyde evolved was titrated with sodium bisulfite, thus permitting quantitative evaluation of the process. It was found that hydrolysis of vinylcaprolactam in a weakly acidic medium, such as approx. 0.2 N sodium bisulfite, only proceeds to the

extent of 30-35%. Addition of 2% sulfuric acid considerably accelerates the reaction, although the degree of completeness depends in large measure on the temperature. A series of experiments was carried out with the objective of developing a method of quantitative determination of vinylcaprolactam on the basis of the hydrolysis reaction. It follows from the relevant data (Table 1) that the percent hydrolysis increases with rising concentration of acid and with rise of temperature. The effect of the latter is particularly marked when working with 2% sulfuric acid. Sufficiently good and reproducible results are obtained at a temperature above 20°. On the basis of a large number of experiments it was shown that the optimum conditions for quantitative determination of vinylcaprolactam by the hydrolysis method are: employment of 2% sulfuric acid at 23-25° and a duration of experiment of 30 minutes.

The data obtained were used for development of a method for quantitative determination of vinylpyrrolidone. It was found that in an acid medium vinylpyrrolidone is hydrolyzed with greater difficulty than is vinylcaprolactam (Table 2). In the course of the investigation it was established that the percent hydrolysis of vinylpyrrolidone increases with rising concentration of acid, with rising temperature and with the duration of the experiment. By varying these three parameters (acid concentration, temperature and time) the most satisfactory conditions for quantitative determination of vinylpyrrolidone were selected. These are: hydrolysis in a medium of 10% sulfuric acid at a temperature of 40-42° for 30 minutes.

It has thus been shown that vinylcaprolactam and vinylpyrrolidone, like vinyl ethers, are susceptible to hydrolysis by an ionic mechanism in an acid medium, vinylcaprolactam being hydrolyzed with greater facility than vinylpyrrolidone.

EXPERIMENTAL

1. Hydrolysis of vinylcaprolactam in a medium of 10% sulfuric acid. The experiment is performed in a three-necked flask fitted with mechanical stirrer, thermometer, nitrogen inlet tube, and reflux condenser connected to four Tishchenko bottles filled with distilled water (40 ml in each) for absorption of acetaldehyde. To 10.0 g vinylcaprolactam [b.p. 86.5-87° (2-2.5 mm); n_D^{20} 1.5130] is added 100 ml 10% sulfuric acid and the mixture is heated. Even at 30° the vinylcaprolactam has gone into complete solution and acetaldehyde is evolved, indicating the start of hydrolysis. The temperature of the reaction mass is then raised to 50-52° and held there for 3 1/2 hours. During this period a weak stream of nitrogen is passed though the system to facilitate removal of the acetaldehyde. The reaction product is neutralized with barium carbonate and the precipitated $BaSO_4$ is filtered off and washed five times with water. The aqueous extracts are added to the main filtrate which is then distilled, first at 16 mm (for removal of the main mass of water) and then in a higher vacuum. The final part of the distillation is carried out in a flask fitted with an ensiform side-tube. The distillation gives 5.89 g caprolactam [b.p. 119-121° (4-4.5 mm); m.p. 67.5-69°]. A mixed test with an authentic specimen of pure caprolactam does not give a melting point depression. In addition 1.79 g resin is isolated. The amount of hydrolyzed vinylcaprolactam is 72.5%. The acetaldehyde was determined in the aqueous solutions collected in the Tishchenko absorbers and in the reaction mass since the acetaldehyde could not be completely eliminated from the mass even with the help of the nitrogen stream. Determinations were effected by Ripper's method [6].

Amount of acetaldehyde found by titration:

In the Tishchenko absorbers	1.521 g
In the reaction mass	1.522 g
Total	3.043 g (calculated amount 3.16 g)

The acetaldehyde was identified as the 2,4-dinitrophenylhydrazone with m.p. 159-161° (no melting point depression in a mixed test with an authentic pure specimen).

2. Quantitative determination of vinylcaprolactam and vinylpyrrolidone. All the determinations were carried out on pure specimens which were kept for not more than 2 days after distillation. The constants of the vinylcaprolactam used were: b.p. 90.5-92° (2.5-3 mm); m.p. 34-35° The constants of the vinylpyrrolidone were: b.p. 74-74.5° (3 mm); $n_D^{19.5}$ 1.5122.

ANALYTICAL PROCEDURE

The experiments were performed in a conical flask with a ground-glass stopper and provided with special glass lugs on which were metal springs which tightly fitted the stopper into the flask. The flask was of 200-250 ml capacity. In the flask were put 20 ml sulfuric acid of known concentration and 25 ml of approx. 0.2 N sodium bisulfite solution. The flask was cooled with ice. Into the cooled mass was introduced an accurately weighed amount (60-90 mg) of the vinyl lactam, the stopper was tightly fitted and the mass was energetically shaken for

5 min, before transferring to a thermostat in which it was kept at the required temperature for the requisite period. The excess of uncombined sodium bisulfite was then titrated with 0.1 N iodine solution. A blank was run in identical conditions. The difference between the amount of iodine consumed in the blank and in the actual analysis was equivalent to the amount of hydrolyzed vinyl compound [7]. Results of complete analyses are set forth in Tables 1 and 2. Out of the large number of experiments we present the data for the most typical determinations.

TABLE 1

Conditions and results of hydrolysis of vinylcaprolactam in presence of sulfuric acid

No. of experiment	Conc. of acid in %	Hydrolysis conditions		Amount of substance found, in % of starting amount
		temperature, °C	duration, in min.	
1	2	10-12	30	62,24 58,56
2	2	23-25	30	99,40 98,20
3	10	10-12	30	96,98 95,75 95,31
4	10	23-25	30	98,86 99,12

TABLE 2

Conditions and results of hydrolysis of vinylpyrrolidone in presence of sulfuric acid

No. of experiment	Conc. of acid in %	Hydrolysis conditions		Amount of substance found, in % of starting amount
		temperature, °C	duration, in min.	
5	2	23-25	30	85,58 84,34 84,46
6	2	40-42	30	95,70 95,96
7	10	10-12	30	57,15 52,66
8	10	23-25	30	89,77 92,67 89,84
9	10	23-25	90	98,47 96,65
10	10	23-25	120	100,18 98,74
11	10	40-42	30	96,76 98,11 100,20

SUMMARY

1. It was established that vinyl lactams are hydrolyzed by an ionic mechanism in presence of sulfuric acid. It was shown, using vinylcaprolactam as starting substance, that the reaction yields lactams and acetaldehyde.

2. A procedure was elaborated for quantitative determination of vinylcaprolactam and vinylpyrrolidone. It was shown that the completeness of the determination depends upon the temperature, the duration of the experiment and the concentration of the acid used.

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Received May 8, 1953

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THE SYNTHESIS OF CYCLOÖCTATETRAENE

S. N. Ushakov and O. F. Solomon

Cycloöctatetraene was first synthesized in 1911-1913 by Willstätter, Waser and Heidelberger [1, 2] by stepwise introduction of double bonds into the 8-membered carbocyclic compound obtained by decomposition of pseudopelletierine. In 1940 Reppe [3,4] obtained cycloöctatetraene from acetylene under pressure in presence of ethylene oxide and nickel cyanide. The latter investigation was the start of a series of publications by Reppe and co-workers in the period 1946-1951 on the synthesis of cycloöctatetraene. The reaction was carried out in an autoclave with intensive stirring in solution in tetrahydrofuran, in presence of complex nickel compounds and ethylene oxide or calcium carbide, under a pressure of 15-20 atm. (of which 6 atm. was created by nitrogen) and at a temperature of 80-70°. After a reaction period of 40-50 hours, cycloöctatetraene could be obtained in a yield of up to 70% of the reacted acetylene, together with other products. The latter are cuprene, benzene (10-15%), higher cyclopolyolefins [$C_{10}H_{10}$ and $C_{12}H_{12}$ (5-15%)] and a small amount of resins insoluble in tetrahydrofuran [5, 6, 7, 8, 9].

Considering the cited reaction conditions to be the optimum ones, Reppe regards tetrahydrofuran as the best solvent. The use of benzene, acetone and ether as solvents leads to lower yields of cycloöctatetraene [5, 10, 11, 12]. In discussing the effect of the type of catalyst on the results of the reaction [5, 11, 13] Reppe claims that the active catalysts are compounds of nickel in which the metal is combined in the form of a complex in a very labile condition, for example nickel cyanide, nickel acetylacetonate, nickel ethyl acetate, nickel oxalylbenzoylterephthaloyl and nickel orthoaminophenol [5, 7, 10, 14].

The employment as catalysts of nickel chloride or nickel bromide, in which the nickel is firmly combined with halogens by an ionic bond, or of nickel terephthalocyanine (a complex compound but with the nickel in firm combination), proved to be unsuitable for the purpose [5]. The use has been reported as catalysts, however, of nickel halides together with ethylene oxide [14], as well as of copper compounds [15]. During the synthesis nitrogen is used as a diluent of the acetylene to prevent possible decomposition of the latter (risk of explosion in the drastic conditions of the reaction) [9, 10, 13].

The employment for cycloöctatetraene synthesis of pressures of the order of 30 atm., i.e. nearly double those recommended by Reppe, is reported in a paper by Raymond [16]. In another publication [17], reviewing Reppe's work, reference is made to Reppe's use of temperatures of 70-150° and pressures of 15-20 atm, although the yield of cycloöctatetraene is not stated (data are also lacking on this point in Reppe's original papers). An earlier paper [18] also refers to the use of high temperatures (70-100°) during the synthesis of cycloöctatetraene from acetylene under pressure. There are indications that the yield of cycloöctatetraene in these conditions is fairly low (36% of the converted acetylene). The other products of the reaction are: benzene, 6%; cuprene, 12%; and resins, 36%. These results are substantially in agreement with those of Cope [19]. In the latter investigation, in which the author followed the reaction conditions recommended by Reppe (temperature of 90°), the yield of cycloöctatetraene was about 50% of the acetylene consumed.

Problems of the synthesis of cycloöctatetraene from acetylene under pressure by a catalytic method are also discussed in a number of papers of a review character. The information given in these papers is mainly a repetition of the material discussed above. It is perfectly obvious that many of the conclusions and suggested possibilities of of synthesis contained in these papers are to some extent exaggerated [20]. In addition to studies concerned with the synthesis of cycloöctatetraene from acetylene under pressure, papers have appeared on the preparation of cycloöctatetraene by other methods. Thus, Cope and Owerberger [21] synthesized cycloöctatetraene from pseudopelletierine. These synetheses are lacking in originality since the methods employed are already known from the synthesis of Willstätter. In another paper [22] a method is described for the preparation of cycloöctatetraene from an 8-membered cyclic dimer of chloroprene.

The mechanism of formation of cycloöctatetraene from acetylene has been inadequately studied. Reppe [5, 10, 11, 13] thinks that the role of the active catalyst is played by labile acetylenic compounds (not isolated in the free state); their formation is promoted by the presence of cyclic oxides (ethylene oxide and tetrahydrofuran). Bergman [23] criticizes Reppe's theory and suggests that the acetylene first dimerizes to vinylacetylene which further dimerizes to cyclic compounds. An entirely different theory is expounded by McKinley [24] who considers

that cyclooctatetraene is formed via complex compounds of nickel with tetrahydrofuran. There is no agreed theory about the mechanism of formation of cyclooctatetraene.

An analysis of the literature data on the synthesis of cyclooctatetraene leads to the following conclusions: a) the synethsis of cyclooctatetraene by the usual recipes and methods of classical organic chemistry is extremely complicated and of little interest for technical purposes; b) the new and highly productive method of synthesis by catalytic polymerization of acetylene under pressure possesses considerable advantages; c) the latter reaction has remined practically without study and trustworthy theories of its mechanism are lacking. Agreement is also lacking as to the optimum temperature of the reaction and the optimum pressure range; the function of various reaction components and the necessity for their introduction have not been established, and so on.

EXPERIMENTAL

The purpose of our research was the examination of the influence of various factors on the course of the polymerization of acetylene with the aim of obtaining maximum yields of cyclooctatetraene when starting from industrial acetylene. A study was made of the influence of the following factors on the yield and rate of formation of cyclooctatetraene during catalytic polymerization of acetylene under pressure: 1) the nature of the solvent for the acetylene; 2) the nature of the catalyst; 3) the amount of catalyst; 4) the content and amount of the acetylene diluent; 5) the type of dehydrating agents; 6) the presence in the sphere of reaction of water and other impurities; 7) the reaction temperature; 8) the method of catalysis; 9) the magnitude of the acetylene pressure.

All the starting materials were subjected immediately prior to their use to careful purification and were characterized by the appropriate method.

The dioxan was distilled over KOH to remove peroxides and then fractionally distilled over sodium to remove traces of moisture. After distillation it had the constants: b.p. 100.4-100.8° (760 mm); n_D^{20} 1.4222 ± 0.0001.

Tetrahydrofuran was purified by the same procedure as for dioxane and had the constants: b.p. 64.5-64.8° (760 mm); n_D^{20} 1.4089 ± 0.0001. The benzene was a cryoscopic grade and was distilled over sodium. After distillation it had the constants: b.p. 80.1° (760 mm); n_D^{20} 1.5017 ± 0.0001. Tetralin was distilled under reduced pressure: b.p. 110° (40 mm); n_D^{20} 1.5402 ± 0.0001. Acetone was purified, dried and distilled, after which it had b.p. 55.5-56.8° (760 mm). Ethylene oxide was distilled over sodium and then had b.p. 10.9-11.2° (760 mm). CaC_2 was specification (GOST)* material. The silica gel was dehydrated by heating at 110° for 8 hours. The $CoCl_2$ was analytical grade material. The phthalic anhydride was pure for analysis. The aluminum acetylacetonate was subjected to recrystallization. The nickel acetylacetonate was sublimed and then had m.p. 218°. Nickel cyanide was tested for absence of Cl ion. The nitrogen was technical material with up to 2% O_2. The acetylene was standard (GOST) grade.

Catalytic Polymerization of Acetylene under Pressure

The reaction vessel was a vertical autoclave of V4A steel, designed for a maximum working pressure of 200 atm. at 500° (working capacity 1 liter). Energetic stirring of the reaction mixture was effected with a stirrer of the rotor type reaching nearly to the bottom of the autoclave and running at 250-300 r.p.m. The temperature in the autoclave was measured with a mercury thermometer and was kept constant to ± 2°, using a cylindrical furnace whose electrical heating was regulated with a rheostat. Experiments were run in the following manner: With the cover removed, the autoclave was charged with the solid and liquid starting materials; the cover was then replaced, the stirrer was started and the tightness of the closure was tested by passing a stream of nitrogen for 30 min. and observing whether the pressure was maintained for 10 to 15 minutes. When this test was completed, the nitrogen was discharged from the autoclave and a stream of acetylene was passed through for 2-3 min. until the oxygen content of the exit gas was not more than 0.5% (the residual pressure was 1.5 atm.) The autoclave was then heated to the required reaction temperature and acetylene was fed in directly from a cylinder until attainment of the requisite pressure. During the reaction the working pressure was regulated by one of the following three methods: 1) Periodic addition of acetylene from the cylinder to offset the fall in pressure due to the reaction; 2) feeding of a constant stream of acetylene from the cylinder during the reaction period; 3) development in the autoclave of a pressure exceeding that in the cylinder (when carrying out the reaction in the absence of a diluent by raising the temperature in the autoclave containing the acetylene dissolved at room temperature. Before each addition of acetylene, samples of the liquid and gas phases were withdrawn. The gas samples were analyzed qualitatively and quantitatively for the following substances: CO_2, to obtain information about the oxidation reactions; R—CHO, to establish the presence of water; unsaturated compounds of the type of vinylacetylene, to gain an insight into the intermediate stages of the reaction; oxygen, to elucidate its influence on the course of the reaction (cuprenization). The liquid phase

* All-Union State Standard.

samples were filtered and the refractive index of the filtrate was determined to an accuracy of 0.0001. The amount of acetylene consumed was calculated with allowance for the free space in the autoclave and for the physical parameters (T and p) and was checked by weighing the autoclave before and after the reaction. The reaction was stopped when the refractive index had reached its maximum (n_D^{20} 1.475 - 1.480 in the case of dioxan) and the pressure had ceased to drop. The reaction products were withdrawn from the autoclave and filtered through a Büchner funnel to separate the cuprene formed during the reaction. Adsorbed liquid products of reaction were extracted from the cuprene in a Soxhlet and the filtrate was rectified under reduced pressure in a nitrogen stream in presence of an inhibitor (hydroquinone). The rectification yielded the following fractions: 1) Solvent – up to 60°; 2) cyclooctatetraene – 60.9° (46.5 mm); 3) still residue: a) yellow liquid with b.p. 96° (5 mm); b) blue liquid, b.p. 135° (5 mm); c) resins insoluble in tetrahydrofuran or in dioxan. The extract from the cuprene was similarly rectified. The rate of rectification was adjusted to enable the cyclooctatetraene to be obtained free from any impurities whatsoever (as verified by the b.p. in vacuum, the n_D^{20} and n_D^{25}).

As a safeguard against oxidation, the cyclooctatetraene isolated in the process was sealed into ampoules under vacuum or in a nitrogen stream; the ampoules were of 50-100 ml capacity and were kept in the dark at 20°. Of the products of the reaction, the cyclooctatetraene was the one subjected to more thorough investigation, while the cuprene was examined less closely. The results of examination of the remaining products of reaction are not considered in this paper.

Influence of nature of solvent on the rate of polymerization of C_2H_2 and the yield of cyclooctatetraene.

The solvents studied in this connection were tetrahydrofuran, dioxan, benzene, tetralin and acetone. All the experiments in which these substances were used as solvents were performed in the following constant conditions: 1) Reaction temperature 85 ± 2°; 2) C_2H_2 pressure 28-12 atm; 3) amount of catalyst 0.6 g calculated on the cation; 4) amount of solvent 100 g; 5) duration of reaction 20 hours; 6) free oxygen content of the autoclave in accordance with GOST limit for C_2H_2 (0.3%). The speed of polymerization was expressed as the number of grams of acetylene polymerized per hour, taking a mean value based on the total reaction period of 20 hours. (The curves in Fig. 1 show the reaction rate at various periods throughout the process.) The results of the experiments are set forth in Tables 1 and 2.

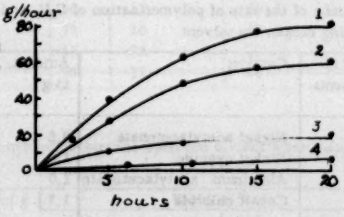

Fig. 1. Dependence of the rate of polymerization of C_2H_2 on the nature of the solvent: 1-dioxan; 2- tetrahydrofuran; 3- benzene; 4- tetralin

Influence of the nature of the catalyst on the reaction rate and the yield of cyclooctatetraene. Catalysts tested in this connection were nickel cyanide, cobalt chloride, aluminum acetylacetonate and nickel acetylacetonate. All the experiments using these catalysts were performed with maintenance of the same constant conditions as in the preceding experiments. The results of the experiments are set forth in Tables 3 and 4 and plotted in Figs. 2 and 3.

Influence of the amount of catalyst on the rate of polymerization of C_2H_2 and on the yield of cyclooctatetraene. Experiments were carried out in the indicated conditions (but with 250 g solvent) with the following amounts of additives: nickel acetylacetonate 15, 7.5 and 3.2 g; nickel cyanide 10 and 3.2 g. Results of the experiments are set forth in Table 5 and plotted in Fig. 4.

Influence of diluent on the rate of polymerization of C_2H_2 and on the yield of cyclooctatetraene. For clarification of the influence of a gaseous, inert diluent on the rate of polymerization under pressure and on the yield of cyclooctatetraene, nitrogen containing 2% oxygen (Orsat determination) was used. All the experiments were performed with maintenance of the following condition: temperature 85 ± 2°, C_2H_2 pressure 28-12 atm.; amount of solvent (tetrahydrofuran) 250 g; amount of ethylene oxide 16 g; total duration of reaction

20 hours; amount of catalyst 0.6 g (calculated on the cation). Results are set forth in Table 6 and plotted in Fig. 5.

TABLE 1

Dependence of the rate of polymerization and yield of cyclooctatetraene on the nature of the solvent when using nickel acetylacetonate as catalyst

Number of experiments	Solvent	Number of grams C_2H_2 per hour	Yield in %		
			C_8H_8	cuprene	remaining* products
3	Dioxan	4.0	72	10	18
2	Tetrahydrofuran	3.0	45	32	23
2	Benzene	1.0	30	30	40
2	Tetralin	0.6	25	25	50

* These are taken to comprise the volatile products of the first fraction, the residue in the still, and losses.

TABLE 2

Dependence of the rate of polymerization and yield of cyclooctatetraene on the nature of the solvent when using nickel cyanide as catalyst

Number of experiments	Solvent	Number of grams C_2H_2 per hour	Yield in %		
			C_8H_8	cuprene	remaining products
2	Dioxan	3.0	68	14	18
3	Tetrahydrofuran	2.0	45	30	25
2	Benzene	0.8	32	30	38
2	Tetralin	0.5	20	25	55

TABLE 3

Dependence of the rate of polymerization of C_2H_2 and the yield of cyclooctatetraene on the nature of the catalyst when using dioxan as solvent

Number of experiments	Catalyst	Amount, in g	No. of g C_2H_2 per hour	Yield in %		
				C_8H_8	cuprene	remaining products
3	Nickel acetylacetonate	3.2	4.0	72	10	18
2	Nickel cyanide	1.5	3.0	68	14	18
2	Aluminum acetylacetonate	1.0	0	0	0	0
2	Cobalt chloride	1.7	0	0	0	0

TABLE 4

Dependence of the rate of polymerization of C_2H_2 and the yield of cyclooctatetraene on the nature of the catalyst when using tetrahydrofuran as solvent

Number of experiments	Catalyst	Amount, in g	No. of g C_2H_2 per hour	Yield in %		
				C_8H_8	cuprene	remaining products
2	Nickel acetylacetonate	3.2	3.0	45	32	23
3	Nickel cyanide	1.5	2.0	45	30	25
2	Aluminum acetylacetonate	1.0	0	0	0	0
2	Cobalt chloride	1.7	0	0	0	0

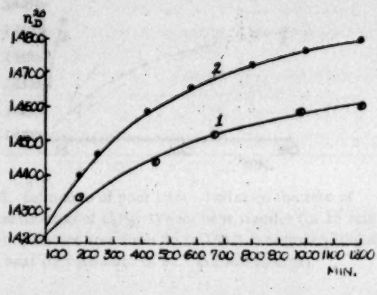

Fig. 2. Dependence of rate of polymerization on the nature of the catalyst (solvent dioxan): 1) nickel cyanide; 2) nickel acetylacetonate

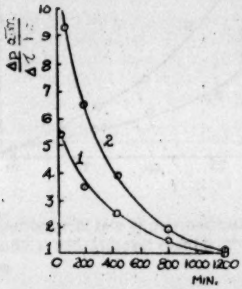

Fig. 3. Dependence of the rate of polymerization of C_2H_2 on the nature of the catalyst (solvent tetrahydrofuran): 1) nickel cyanide; 2) nickel acetylacetonate

TABLE 5

Dependence of velocity of polymerization of C_2H_2 and the yield of cycloöctatetraene on the amount of catalyst when using dioxan as solvent

Number of experiments	Catalyst	Amount, in g	No. of g C_2H_2 per hour	Yield in %		
				C_8H_8	of cuprene	of remaining products
2	Nickel acetylacetonate	15	12.6	38	27	35
2	Nickel acetylacetonate	7.5	10.5	58	17	25
6	Nickel acetylacetonate	3.2	9.5	70	10	20
2	Nickel cyanide	10	9	45	35	20
5	Nickel cyanide	3.2	8.2	70	12	18

TABLE 6

Dependence of rate of polymerization of C_2H_2 and of yield of cycloöctatetraene upon the diluent when using nickel cyanide as catalyst

Number of experiments	Diluent	Amount, in %	No. of g C_2H_2 per hour	Yield in %		
				C_8H_8	of cuprene	of remaining products
2	Nitrogen	0	8.80	45	30	25
2	Nitrogen	10	6.0	43	28	29
3	Nitrogen	30	3	45	27	30
2	Nitrogen	50	2	45	32	23

Influence of nature of dehydrating media on the rate of polymerization of C_2H_2 and on the yield of cycloöctatetraene. The following compounds were studied: ethylene oxide, calcium carbide, silica gel, and phthalic anhydride. The dehydrating agents were introduced in the amount of 6% calculated on the solvent. The amount of solvent was 100 g. The remaining reaction conditions were the same as in the preceding experiments. Results are set forth in Tables 7 and 8. Silica gel and phthalic anhydride had no appreciable influence upon the reaction course.

Influence of water and other impurities on the rate of polymerization of C_2H_2 and on the yield of cycloöctatetraene. The qualitative effect of water and other impurities on the rate of polymerization of C_2H_2 was studied in all the experiments while maintaining constant conditions with introduction of 250 g solvent. The results of these experiments are set forth in Table 9.

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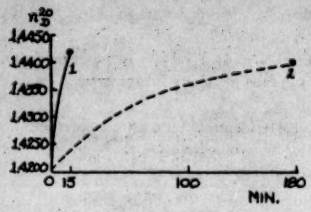

Fig. 6. Influence of poor heat transfer on the rate of polymerization of C_2H_2: 1) poor heat transfer (in 15 min. the temperature rose from 85 to 150°) 2) normal withdrawal of heat (temperature of 85 ° did not change)

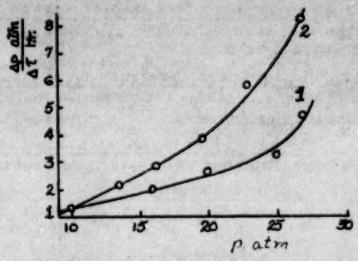

Fig. 7. Dependence of rate of polymerization of C_2H_2 on the pressure at 85°: 1) nickel cyanide; 2) nickel acetylacetonate

TABLE 9

Dependence of rate of polymerization of C_2H_2 and the yield of cyclooctatetraene on the presence of impurities

Number of experiments	Water or other impurities	Solvent	Catalyst	Grams of C_2H_2 per hour	Yield of C_2H_2, in %
2	Water	Tetrahydrofuran	Nickel cyanide	0	0
2	Non-dehydrated solvent	Dioxan	Nickel cyanide	6.7	55
2	Undistilled solvent	Dioxan	Nickel cyanide	5.7	50
2	Air dry catalyst	Dioxan	Nickel acetyl-acetonate	2.7	45

TABLE 10

Dependence of rate of polymerization of C_2H_2 and yield of cyclooctatetraene on the thermal regime when using nickel cyanide as catalyst

Number of experiments	Temperature in °C	Grams of C_2H_2 per hour	Yield, in %		
			C_2H_2	of cuprene	of remaining products
3	95-116	13	35	40	25
3	90-95	10	40	35	25
4	85	8.8	43	30	27
3	75	5	45	32	23
2	65	3	48	25	27

TABLE 11

Dependence of rate of polymerization of C_2H_2 on the pressure

Nickel acetylacetonate			Nickel cyanide		
Number of experiments	Pressure in atm.	$\Delta P/\Delta t$ at 85°	Number of experiments	Pressure in atm.	$\Delta P/\Delta t$ at 85°
5	27	8,10	4	27	4,60
3	23	5,77	3	23	3,0
4	19,7	3,80	4	19,7	2,45
4	16,3	2,15	3	16,3	2,0
3	13,6	2,15	3	13,6	1,40
3	10	1,40	3	10,0	1,30

Influence of reaction temperature on the rate of polymerization of C_2H_2 and on the yield of cyclooctatetraene. All the experiments for study of the temperature effect were performed in tetrahydrofuran (250 g) with introduction of ethylene oxide (6%). Results are set forth in Table 10 and plotted in Fig. 6.

Influence of pressure on the rate of polymerization of C_2H_2. In experiments for clarification of the influence of the pressure, the solvent used was dioxane (250 g) in otherwise identical conditions. Results of the experiments are set forth in Table 11 and plotted in Fig. 7.

Results of analysis of the reaction products. Fully identical results were obtained in all the above experiments; the following constants were found, for example, for cyclooctatetraene:

Our data	Reppe's data
B.p. 60° (46.5 mm); n_D^{20} 1,5342;	B.p. 60° (46.79 mm); n_D^{20} 1,5290;
M.p. 6.5; mol. wt. 103.4; d_4^{20} 0.9200	M.p. 7°; mol. wt. 103.5; d_4^{20} 0,9206.

Data for analysis of cyclooctatetraene:

Found %: C 92.25; H 7.98
Calculated %: C 92.30; H 7.70

Data for analysis of cuprene:

Found %: C 62.51; H 6.63; ash 28.41

Neither in the cold nor after prolonged extraction whilst heating did cuprene go into solution in any of the common organic solvents or in dilute and concentrated inorganic acids.

EVALUATION OF RESULTS

As already mentioned, the aim of the present paper was to study the synthesis of cyclooctatetraene by catalytic polymerization of acetylene under pressure for the purpose of characterization of the influence on the course of the reaction and on the yield of cyclooctatetraene of the main physicochemical factors. Since in none of the previously published literature is there a characterization of the principal raw material employed (acetylene) or any mention of the purification of acetylene under pressure, we used technical acetylene which proved to be suitable for this reaction. Our attempts to reproduce the synthesis of cyclooctatetraene by the procedure described by Reppe did not give satisfactory results. This led us to doubt the expediency of making use in the investigation of many of the basic data published in the literature as a basis of the investigation.

The solvents used in an examination of the influence of different solvents on the course of the reaction were dioxan, tetrahydrofuran, benzene, tetralin and acetone. Tetrahydrofuran was included in the tests because it was necessary to check the literature data according to which tetrahydrofuran is the best solvent for the process in question. Benzene was used as a representative of the aromatic hydrocarbons. During the investigation, the literature data were confirmed according to which tetrahydrofuran is a better solvent for this process than benzene, acetone or tetralin, but the claims that it was the best solvent in general were refuted, since the best synthesis results both in regard to the reaction velocity and to the yield of cyclooctatetraene were attained when using (for the first time in this reaction) dioxan as the solvent, as clearly shown by Fig. 1.

Consequently the intensification of the effect of the functional groups of the cyclic ether led to intensification of the reaction. The more pronounced hydrocarbon character of the solvent resulting from replacement of tetralin by benzene led to diminution of the activity of the reaction course. Employment of a catalyst soluble in the liquid phase (in the case of homogeneous catalysis) appreciably intensifies the reaction. Consequently nickel acetylacetonate slows down the higher velocity of the reaction without substantially reducing the yield of product. It should be noted that the literature reports in all cases recommend the use of nickel cyanide but evidently without realizing the implications of the foregoing observations. Apart from the nickel catalysts mentioned above, we also tested a few other compounds. To test the possibility of using as catalysts elements in the same group of the periodic system as nickel i.e. possessing a similar electronic configuration, $CoCl_2$ was used. In experiments with the latter, however, not even traces of cyclooctatetraene were obtained nor, in general, any signs of reaction of acetylene at all.

Experiments with another compound – aluminum acetylacetonate – as catalyst were performed with the aim of testing the influence of the anionic component of a catalyst on the course of the reaction. Substitution of nickel by aluminum, however, in nickel acetylacetonate – the best of all the catalysts studied – leads to complete disappearance of the catalytic action. This fact appears to us to be evidence that the anion does not play any independent catalytic role in this reaction. The intensification of the catalytic activity when nickel acetylacetonate is substituted for nickel cyanide is evidently due to a change in the character of the catalysis (homogeneous in the latter case and heterogeneous in the former). Thus the creation of conditions of homogeneous catalysis is preferable and permits a considerable reduction of the duration of reaction. Concerning, on the other hand, the amount of catalyst, its

effect is developed in the following manner: Both in the case of heterogeneous catalysis (nickel cyanide) and of homogeneous catalysis (nickel acetylacetonate), an increase in the amount of catalyst (using the same amount of solvent) causes the reaction velocity to increase, but at the same time the yield of cyclooctatetraene is lowered. It is characteristic that when using nickel acetylacetonate the increase in the amount of catalyst brings about a drop in yield of cyclooctatetraene which is associated with increased yields of both cuprene and the remaining products, whereas when using nickel cyanide the reduced cyclooctatetraene yield is bound up in the main with higher yields of cuprene only. On the basis of comparison of the results of the individual experiments we can recommend optimum ratios of solvent and catalyst which will guarantee an adequate yield at a satisfactory reaction velocity. Addition of nitrogen considerably lowers the reaction velocity. Our numerous experiments showed that the process is perfectly free from hazards even when using undiluted acetylene if our safety procedure is strictly observed.

New data that we have obtained, especially when working in the absence of a diluent, vividly demonstrate that the application of all the conditions of synthesis used by other investigators is by no means essential. These data even showed the opposite: certain factors of synthesis described in the literature prove to have a negative influence on the course of the process. This fact is even more strikingly manifested by a critical evaluation and check of the need for using such completely necessary (in Reppe's opinion) reaction components as ethylene oxide and calcium carbide. It was actually found that the omission of these compounds during the synthesis affords the possibility of obtaining higher yields of cyclooctatetraene at a relatively small decrease of reaction velocity. Consequently neither ethylene oxide nor calcium carbide are indispensable components of the reaction and their interchangeability is the possible result of their greater or lesser inertness in respect of the reaction. In the light of these facts the assertion of Reppe that ethylene oxide plays a decisive part in the mechanism of formation of cyclooctatetraene does not bear criticism.

The purity and dryness of the starting materials play an important part in the polymerization of acetylene to cyclooctatetraene under pressure. Water completely inhibits the reactions. Use of undried starting materials shows down the reaction and leads to reduced yields. Impurities in the catalyst have a similar effect and thorough purification is therefore necessary.

The high exothermal effect of the reaction makes absolutely essential the strict maintenance of the correct temperature regime and of the conditions for normal heat removal. A rise of temperature to 85° has no appreciable effect on the yield but leads to a considerable increase of reaction rate. The yield of cyclooctatetraene only falls markedly when the temperature rises above 85°. Thus the optimum temperature ensuring a sufficiently high reaction rate in association with maximum yield of cyclooctatetraene is about 85°. A rise of the initial pressure exerts a similar influence on the reaction rate to that of temperature rise. A threefold increase of the pressure leads to an approximately 3½ - fold increase in the velocity of the homogeneous catalytic reaction. In that case, however, the increased rate does not lower the yield. It is consequently expedient to conduct the process at a constant pressure of the order of 25-28 atm, which necessitates a constant flow of acetylene into the reaction vessel. The production during the polymerization of acetylene of any particular compound as main product, in a substantial yield, is governed by the choice of such conditions of performance of the reaction and of bringing together of the reaction components as will ensure that the required direction of the reaction becomes the predominant one while all the other directions are inhibited to the maximum extent. The occurrence of side reactions in our experiments led to the appearance in greater or lesser degree of the following in the reaction product: cyclooctatetraene, cuprene, benzene, styrene, a yellow product of unknown structure, with b.p. 96° (5 mm), a blue product of unknown structure with b.p. 135° (5 mm) and several other more volatile or higher molecular compounds. According to the literature data, the same process, but in somewhat different conditions, led to formation of higher cyclopolyolefins.

These diverse directions of the process are the result of the effect of a large number of factors. There are, however, two main competing directions of the reaction: the formation of cyclooctatetraene and the formation of cuprene, and these have also been studied in our research. If it were possible to regulate the process to yield only these two products, the problem could be regarded as substantially solved, for the amount of all the remaining products of the reaction is relatively small. But the mastery of even these two directions of the reaction is quite a difficult problem, and even though our investigation has shown that it is possible in practice to conduct the process in the required direction, the theoretical aspects of the problem remain unclarified. The greatest difficulties in the theoretical investigation of the characteristics of the process arise when we consider the mechanism of the reaction.

Our experimental data refute the mechanism proposed by Reppe which involved formation of an active catalyst (nickel acetylide), starting from the presence of ethylene oxide in the sphere of reaction, since it was shown that the reaction also proceeds in the absence of ethylene oxide. Any other more acceptable mechanism of the reaction has not yet been advanced.

SUMMARY

1. The polymerization of acetylene under pressure in presence of catalysts proceeds with formation of various compounds. The particular direction followed by the reaction, and consequently also the yield of cyclooctatetraene, depends on the reaction conditions (nature of solvent, catalyst, temperature, pressure, presence of additives, etc.)

2. The type of catalysis plays an important part in regard to the course of the process, especially in connection with the reaction velocity. The homogeneous catalysis which we carried out has substantial advantages over heterogeneous catalysis as used by Reppe.

3. A non-hazardous course of the reaction can be achieved without resorting to special dilutions of the acetylene (e.g. with nitrogen), by conducting the reaction in presence of the vapor of those liquids which enable precise maintenance of the reaction regime.

4. Technical acetylene may be used both for the practical production of cyclooctatetraene and for investigation of the main characteristics of the process.

5. In a series of studies of solvents, the best results are got with dioxan (used by us for the first time for this reaction) which has definite advantages over the best of the solvents described in the literature (tetrahydrofuran), particularly in respect of reaction velocity.

6. Nickel acetylacetonate, which acts homogeneously in a dioxan medium, is a more active catalyst than nickel cyanide. The activity of the catalyst (in the heterogeneous process) decreases due to additional cuprene formation and deposition of carbon black.

The process of cuprenization is intensified with increasing amount of catalyst in presence of ethylene oxide and calcium carbide, also on rise of temperature to 90-100°. The poor heat conduction combined with the strong exothermicity of the process leads to a marked temperature rise and to nearly complete transformation of the acetylene into cuprene. The optimum reaction temperature is between 82 and 87°.

7. The polymerization of acetylene to cyclooctatetraene proceeds in the absence of ethylene oxide and calcium carbide. Introduction of the latter compounds is not only unnecessary but is even detrimental to the process (slight reduction in the yield of cyclooctatetraene).

8. Inhibitors of the reaction are traces of water and impurities (of undetermined chemical structure) present in the catalyst.

9. The yield of cyclooctatetraene increases with increasing pressure in the reaction space.

10. A yield of over 70% cyclooctatetraene is attained with good reproducibility of individual experiments and high reaction velocity.

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Received July 6, 1953

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ORGANOSILYL ESTERS OF ACETIC AND ISOBUTYRIC ACIDS

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Organosilyl esters of the general formula $R_3SiOOCR'$ have received only cursory study. Descriptions have been published of only four esters of acetic acid containing, as the radical R, methyl [1, 2, 3], ethyl [4], n-propyl [5] or phenyl [6, 7] groups, and of only one each of the esters of butyric, isovaleric and enanthic acids in which R was the ethyl radical [8]. Complex organosilicon esters of the general formula $R_2R''SiOOCR'$ have not previously been described. In this paper we present the properties of four esters, synthesized for the first time, of acetic and isobutyric acids of the type of $R_2R''SiOOCR'$ and $R_3SiOOCR'$.

All the esters were prepared by reaction of anhydrous sodium acetate or isobutyrate with R_3SiCl or $R_2R''SiCl$ by heating for 10-15 hours in a medium of dry ligroine at 60-85° with energetic stirring. After separating the precipitated NaCl and the excess of organic acid salt, the ester was isolated in the pure form by repeated vacuum fractionation in a current of dry air. All the prepared esters were transparent, colorless, easily hydrolyzed (by water) liquids of faint odor. The starting R_3SiCl and $R_2R''SiCl$ were obtained by the action of RMgBr on $SiCl_4$ or methylchlorosilane. $(C_4H_9)_3SiCl$ was prepared by the action of n-C_4H_9MgBr on $SiCl_4$ and was isolated in the pure form by decomposition of the butylsiloxanes with freshly sublimed $AlCl_3$ [9]. $CH_3(C_4H_9)_2SiCl$ was prepared by a similar method; action of n-C_4H_9MgBr on CH_3SiCl_3. Symmetrical dimethyltetra-n-butyldisiloxane was obtained as intermediate product.

Silicon was determined by ashing a weighed amount of substance with a mixture of conc. HNO_3 and H_2SO_4; chlorine by direct titration with 0.1 N NaOH in presence of phenolphthalein; the ester number by saponification with KOH solution in diethylene glycol [10]; the molecular refraction was calculated by Warrick's method [11].

EXPERIMENTAL

Methyldi-n-butylsilyl acetate $CH_3(C_4H_9)_2SiOOCCH_3$ was prepared from 45 g (0.23 mole) $CH_3(C_4H_9)_2SiCl$ and 30 g (0.37 mole) CH_3COONa. Yield about 70%; b.p. 83° (8 mm); n_D^{20} 1.4284; d_4^{20} 0.8568; found M 206; calculated M 216.3; found MR 65.0; calculated MR 63.45. found ester number 261,267; calculated 259.2.

Found %: Si 12.52; 13.2

$C_{11}H_{24}O_2Si$. Calculated %: Si 12.96

Methyldi-n-butylsilyl isobutyrate $CH_3(C_4H_9)_2SiOOCCH(CH_3)_2$ was prepared from 30.5 g (0.2 mole) $CH_3(C_4H_9)_2SiCl$ and 33.2 g (0.3 mole) $(CH_3)_2CHCOONa$. Yield about 60%; b.p. 105-107° (5 mm); 134-140° (20 mm); n_D^{20} 1.4238; d_4^{20} 0.8620; found mol. wt. 249, calc. 244.4; found MR 72.32; calculated MR 72.71; found ester number 218; calculated 229.5.

Found %: Si 10.77

$C_{13}H_{28}O_2Si$. Calculated %: Si 11.47

Tri-n-butylsilyl isobutyrate $(C_4H_9)_3SiOOCCH(CH_3)_2$ was prepared from 25 g (0.1 mole) $(C_4H_9)_3SiCl$ and 25 g (0.22 mole) $(CH_3)_2CHCOONa$. Yield 61%; b.p. 145-146° (13 mm); 160° (20 mm), n_D^{20} 1.4345; d_4^{20} 0.8663; found molecular weight 280.8; 291; calculated 286.5; found MR 86.21; calculated MR 86.60; found ester number 199.3; 205.8; calculated 202.9.

Found %: Si 9.38; 9.55

$C_{16}H_{34}O_2Si$. Calculated %: Si 9.79

Dimethylphenylsilyl isobutyrate $(CH_3)_2C_6H_5SiOOCCH(CH_3)_2$ was prepared from 20 g (0.11 mole) $(CH_3)_2C_6H_5SiCl$ and 25 g (0.22 mole) $(CH_3)_2CHCO \cdot ONa$. Yield of pure ester 10%; b.p. 114-116° (6 mm); n_D^{20} 1.4909; d_4^{20} 0.9844; found mol. wt. 215; 218; calculated 222.3; found MR 65.4; calculated MR 64.75; found ester number 249; calculated 252.3.

Found %: Si 12.1; 12.28

$C_{12}H_{18}O_2Si$. Calculated %: Si 12.62

Methyl-n-butylchlorosilane $CH_3(C_4H_9)_2SiCl$ was prepared from $n\text{-}C_4H_9MgBr$ and CH_3SiCl_3 in the ratio of 2:1; b.p. 193-198°; n_D^{20} 1.4325; d_4^{20} 0.8656; found MR 57.73; calculated MR 58.0.

	Found %:	Cl 18.3
$C_9H_{21}SiCl$.	Calculated %:	Cl 18.45

Symmetrical dimethyltetra-n-butyldisiloxane $[CH_3(C_4H_9)_2Si]_2O$ was isolated from the products of hydrolysis and dehydration of methyl-n-butylchlorosilane (V). B.p. 150-152° (5 mm); n_D^{20} 1.4336; d_4^{20} 0.8281; found mol. wt. 345; 347; calculated 330.6; found MR 103.7; calculated MR 104.48.

	Found %:	Si 16.98; 17.1
$C_{18}H_{42}OSi_2$.	Calculated %:	Si 16.95

SUMMARY

1. The following 4 new organosilyl esters were synthesized by reaction of the Na salts of acetic and isobutyric acids with alkylchlorosilanes: methyldi-n-butylsilyl acetate; methyldi-n-butylsilyl isobutyrate; tri-n-butylsilyl isobutyrate; and dimethyldiphenylsilyl isobutyrate.

2. Intermediate compounds obtained were the previously undescribed methyldi-n-butylchlorosilane and symmetrical dimethyltetra-n-butyldisiloxane.

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Received July 17, 1953

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* See Consultants Bureau Translation, p. 121.

THE OPTICAL METHOD OF INVESTIGATION OF HYDROCARBONS

COMMUNICATION 7. RAMAN SPECTRA OF SOME NAPHTHENES

P. A. Bazhulin, A. V. Koperina, A. L. Liberman, V. A. Ovodova and B. A. Kazansky

The present investigation is one of a series on the scattering spectra of pure hydrocarbons systematically carried out in the laboratories of the Institute of Physics and the Institute of Organic Chemistry of the Academy of Sciences of the USSR since 1939 [1-6].

The hydrocarbons hitherto examined were mainly those boiling within the range of 28 and 130° and whose Raman spectra can already serve as a basis for analysis of the individual composition of the most important fractions of straight-run gasolines. The list of investigated hydrocarbons presenting interest from the view point of analysis of gasolines in the indicated temperature range is, however, still incomplete: up to now we have studied all the liquid paraffinic hydrocarbons containing 5 to 8 carbon atoms and some of the nonanes, while of the naphthenes we have only studied those most frequently encountered in petroleums. In the present paper we set forth data for another seven naphthenes which are difficult to synthesize and which have boiling points between 108 and 142°.

In previous communications [1-5] exploratory spectral data were submitted for a series of hydrocarbons which for one reason or another were insufficiently pure. Subsequently a considerable number of these hydrocarbons were synthesized afresh and purified more thoroughly. Starting with the present communication, we shall set forth data about changes which ought to be made in previously published results. Thus, in the present paper we give details of spectra of freshly synthesized and extremely pure trans-1,4-dimethylcyclohexane, which supersede the earlier data for this preparation based on material containing an appreciable amount of the cis-form; in addition we publish new data for the spectra of newly synthesized n-octane and 2,5-dimethylhexane.

The apparatus and experimental procedure were described in previous communications [1,2,3]. The intensities of the spectral lines at the maxima were determined by the method of photographic photometry. Since all results were obtained in identical conditions, the new data are comparable with those previously published.

RESULTS OF MEASUREMENTS

Below we present the results of studies of the frequency and intensity of the spectra of eight naphthenes with b.p.s between 108 and 142°. For each hydrocarbon a brief description is given of the method of preparation and of the main physical properties (b.p., refractive index, density, and molecular refraction, both found and calculated); all the constants are compared with those of extremely pure preparations of the respective hydrocarbons [7] (given in square brackets), apart from 1,2-dimethyl-4-ethylcyclopentane which was obtained for the first time. The following symbols are used to characterize the Raman lines: br – broad; d – double; r – sharp; ba – line set against a background of considerable intensity; (?) – the possibility is not excluded that the line in question is a repetition of a certain line excited by another one.

Cis, trans, cis-1,2,4-trimethylcyclopentane* was prepared from 2,4-dimethylcyclopenten-2-one which was synthesized by Nazarov's method [8]. The ketone was hydrogenated in presence of skeletal nickel to 2,4-dimethylcyclopentan-1-ol; the latter was oxidized to 2,4-dimethylcyclopentan-1-one which with methylmagnesium iodide was converted to the tertiary alcohol; from the latter by dehydration followed by hydrogenation, of the unsaturated hydrocarbon and fractionation of the hydrogenation products in a column of 60 theoretical plates were isolated cis, trans,cis-1,2,4-trimethylcyclopentane and the below-described cis,cis,trans-1,2,4-trimethylcyclopentane: b.p. 109.2° (760 mm); n_D^{20} 1.4101; d_4^{20} 0.7463; found MR 37.23; calc. for C_8H_{16} MR 36.94 [B.p. 109.28° (760 mm); n_D^{20} 1.41057; d_4^{20} 0.74727.

$\Delta\nu$: 257 (7), 275 (3, br), 331 (0), 405 (5), 422 (5, br), 490 (15, br), 529 (7), 585 (1, br), 769 (44), 811 (8), 824 (8), 836 (2, br), 938 (8), 966 (2), 999 (1), 1027 (3), 1052 (5), 1079 (4), 1093 (2, br), 1148 (13, d), 1225 (0), 1253 (0), 1280 (1), 1308 (6), 1341 (7), 1359 (3), 1459 (48), 2665 (0), 2725 (10), 2848 (90), 2868 (180), 2904 (30, ba), 2925 (130), 2955 (160).

Cis,cis,trans-1,2,4-trimethylcyclopentane was prepared at the same time as the preceding hydrocarbon and separated by fractional distillation. B.p. 116.8° (760 mm); n_D^{20} 1,4185; d_4^{20} 0.7632; found MR 37.06, calculated

* See Diagram A, p. 608.

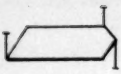


Diagram A

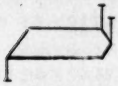


Diagram B

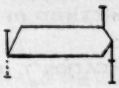


Diagram C

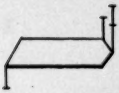


Diagram D

for C_9H_{16} MR 36.94. [B.p. 116.73° (760 mm); n_D^{20} 1.41854; d_4^{20} 0.76345.] (See Diagram B above.)

$\Delta\nu$: 241 (0), 289 (3, br), 370 (3), 418 (0), 436 (2, br), 498 (14), 520 (9), 748 (17, br), 761 (20), 812 (0), 854 (6), 895 (0), 938 (8), 975 (2), 1023 (3), 1037 (2, br), 1066 (2), 1091 (2), 1148 (5), 1172 (6), 1228 (0), 1313 (8), 1347 (5), 1379 (0), 1459 (44, br), 2729 (5), 2851 (60), 2873 (160), 2904 (100), 2935 (150), 2961 (120).

Cis,cis,trans,1,4-dimethyl-2-ethylcyclopentane.* 2,4-Dimethylcyclopentan-1-one was prepared by the previously described method; from it by the action of ethylmagnesium bromide was obtained the tertiary alcohol which was converted into the unsaturated hydrocarbon as above and then into a mixture of the stereoisomers of 1,4-dimethyl-2-ethylcyclopentane; the latter were fractionated in a column with an efficiency of 80 theoretical plates. Cis,cis,trans-1,4-dimethyl-2-ethylcyclopentane was isolated with b.p. 136.5° (760 mm); n_D^{20} 1.4205; d_4^{20} 0.7637; found MR 41.84; calculated for C_9H_{18} MR 41.56. [The literature does not contain any data for the properties of this hydrocarbon.] (See Diagram C above.)

$\Delta\nu$: 191 (0, br), 264 (2, br, d), 317 (2), 372 (0, br), 402 (1), 420 (5), 445 (3), 483 (5), 524 (3), 560 (0), 746 (2, d), 772 (7), 796 (5), 819 (4, br), 841 (4, br), 927 (0, br), 954 (4), 972 (4), 1043 (6), 1055 (6), 1079 (1), 1095 (2, br), 1149 (9, br), 1198 (0), 1250 (1), 1285 (3), 1311 (3, br), 1348 (6), 1362 (2), 1447 (30), 1462 (55), 2729 (5), 2853 (80), 2870 (160), 2902 (90), 2933 (120), 2958 (120).

Cis,trans,cis-1,4-dimethyl-2-ethylcyclopentane was prepared together with the preceding hydrocarbon and isolated by fractional distillation. B.p. 143.2° (760 mm); n_D^{20} 1.4270; d_4^{20} 0.7795; found MR 41.55; calculated for C_9H_{18} MR 41.56. [There are no data for the properties of this hydrocarbon in the literature.] (See Diagram D above.)

$\Delta\nu$: 200 (0, br), 286 (1), 325 (4), 376 (0, br), 392 (3), 416 (3), 435 (0), 474 (3), 501 (2), 516 (4, br), 536(0), 745 (5), 761 (10), 792 (5), 809 (4), 855 (6), 907 (1), 922 (2), 964 (6, d), 1025 (1), 1042 (8), 1066 (4), 1092 (3), 1150 (5), 1164 (6), 1191 (0), 1228 (1), 1260 (2), 1287 (3), 1313 (4, br), 1361 (4, d), 1445 (20), 1460 (55), 2729 (5), 2854 (70), 2872 (170), 2902 (50), 2935 (180), 2959 (130).

1,1,3-Trimethylcyclopentane was obtained from β-methylcyclopentanone; treatment with methylmagnesium iodide gave the tertiary alcohol which was then converted to the chloride; the latter by reaction with zincdimethyl was transformed into 1,1,3-trimethylcyclopentane. The hydrocarbon was purified by passing through silica gel and was then distilled in a column with an efficiency of 40 theoretical plates. B. p. 105.1° (760 mm); n_D^{20} 1.4110, d_4^{20} 0.7484; found MR 37.20; calculated for C_8H_{16} MR 36.94 [B.p. 104.89° (760 mm); n_D^{20} 1.41115; d_4^{20} 0.74825.]

$\Delta\nu$: 241 (0), 290 (6), 343 (11), 409 (7), 443 (0), 531 (13), 570 (7), 746 (11), 792 (17), 808 (5), 846 (0, br), 936 (11, d), 982 (6), 993 (8), 1041 (1, br), 1059 (4), 1092 (4), 1131 (2), 1176 (7), 1192 (7), 1235 (7, br), 1311 (7), 1351 (1), 1446 (20), 1463 (33), 2718 (10), 2756 (2), 2860 (130), 2893 (80), 2924 (130), 2956 (170).

Trans-1-methyl-3-ethylcyclopentane was prepared from β-methylcyclopentanone; reaction with ethylmagnesium bromide converts it into the tertiary alcohol; the latter is dehydrated and the resultant unsaturated hydrocarbon is hydrogenated and fractionated in a column with an efficiency of 40 theoretical plates. B.p. 120.1° (753 mm); n_D^{20} 1.4185; d_4^{20} 0.7626; found MR 37.09; calculated for C_8H_{16} MR 36.94. [Cis-form, b.p. 120.2° (760 mm); n_D^{20} 1.420; d_4^{20} 0.772. Trans-form: b.p. 120.8° (760 mm); n_D^{20} 1.4186; d_4^{20} 0.7619.]

$\Delta\nu$: 284 (2, br), 303 (4), 394 (14), 425 (5, br), 522 (5), 538 (3), 596 (0), 760 (2, br), 774 (4, br), 837 (18, br), 912 (0), 939 (4), 982 (2), 992 (4), 1007 (2, br), 1040 (5), 1068 (4, br), 1099 (3, br), 1134 (4), 1152 (4), 1176 (0, br), 1248 (1, br), 1284 (3), 1313 (3), 1330 (1), 1355 (3), 1448 (43), 1464 (30), 2729 (5), 2845 (90), 2889 (180), 2903(90), 2927 (130), 2955 (150).

* Contamination with the cis,trans,trans-form is possible. The structure of the cis,cis,trans-form is shown on the diagram by the dense lines; the structure of the cis,trans,trans-form is shown by the broken line.

Cis-1,4-dimethylcyclohexane was prepared by hydrogenation of p-xylene and after passage through silica gel it was separated from the mixture of sterolsomers by fractionation in a column with an efficiency of 75 theoretical plates. B. p. 124,5° (760 mm); n_D^{20} 1,4297; d_4^{20} 0,7829; found MR 36,98; calculated for C_8H_{16} MR 36,94. [B.p. 124,321° (760 mm); n_D^{20} 1,42966; d_4^{20} 0,78285.]

$\Delta\nu$: 125 (4), 258 (4), 286 (1), 310 (2), 373 (12, d), 434 (3), 472 (19, d), 637 (18), 760 (95), 788 (17), 897 (0), 925 (3), 954 (15), 976 (8), 1001 (10), 1055 (23), 1095 (10), 1107 (10), 1160 (10), 1170 (10), 1207 (11), 1248 (6), 1263 (23), 1301 (5), 1319 (2), 1344 (13), 1375 (1, br), 1438 (29), 1463 (34), 2668 (0, d), 2724 (3), 2750 (3), 2852 (170), 2873 (50, ba), 2897 (160, ba), 2912 (150, ba), 2929 (200), 2959 (80, br).

Trans-1,3-dimethylcyclohexane * was obtained together with the preceding hydrocarbon and was isolated by fractionation; b.p. 119,5 (760 mm); n_D^{20} 1,4209; d_4^{20} 0,7627; found MR 37,30; calculated for C_8H_{16} MR 36,94 [B. p. 119,351° (760 mm); n_D^{20} 1,42090; d_4^{20} 0,76255.]

$\Delta\nu$: 254 (0), 335 (0), 376 (50), 429 (0), 454 (32), 475 (15), 547 (0), 566 (0), 760 (150), 786 (6), 849 (0), 926 (3), 953 (11), 1005 ? (4), 1062 (75), 1104 (0), 1166 (20), 1186 (20), 1250 (36), 1264 (2), 1307 (12), 1348 (27), 1361 (15, br), 1436 (13), 1460 (60), 2676 (2, br), 2723 (3), 2748 (1), 2845 (230), 2868 (180), 2911 (120, br), 2926 (230), 2955 (110).

n-Octane** was obtained from 2-octanone, distilled in vacuum in a column with an efficiency of 60 theoretical plates, by dehydration over alumina and hydrogenation over platinized carbon in a duck. The n-octane was fractionated in a column with an efficiency of 60 theoretical plates and has b.p. 125,6-125,7° (760 mm); n_D^{20} 1,3975; d_4^{20} 0,7027; found MR 39,19; calculated for C_8H_{18} MR 39,14. [B. p. 125,667 (760 mm); n_D^{20} 1,39745; d_4^{20} 0,70260.]

$\Delta\nu$: 282 (16), 300 (2, br), 352 (0), 377 (0), 400 (0), 427 (0), 507 (0, br), 707 (0), 730 (0), 766 (1), 813 (2, br), 842 (3), 860 (6), 877 (7), 895 (8), 954 (2, br), 969 (4), 1028 (5), 1044 (5), 1062 (8, r), 1085 (11), 1137 (7), 1165 (2), 1304 (15), 1440 (30), 1459 (30), 2637 (0), 2670 (0), 2732 (5), 2853 (100), 2878 (130, r), 2904 (100, d, ba), 2939 (80), 2964 (45).

2,5-Dimethylhexane*** was prepared by the Würtz method from isobutyl bromide; it was purified from bromides by shaking with ethanolamine and was distilled in a column with an efficiency of 50 theoretical plates; b.p. 109,4° (760 mm); n_D^{20} 1,3925; d_4^{20} 0,6934; found MR 39,27; calculated for C_8H_{18} MR 39,14. [B. p. 109,106° 760 mm); n_D^{20} 1,39246; d_4^{20} 0,69355.]

$\Delta\nu$: 267 (11, br), 314 (9), 433 (6, br), 451 (8), 683 (0), 725 (0), 764 (0), 777 (10), 798 (2), 825 (5), 839 (31), 881 (1), 907 (5, br), 941 (5), 961 (16), 1037 (3), 1048 (6) 1096 ? (2), 1148 (14), 1172 (14), 1232 (2, br), 1293 (5), 1305 (6), 1338 (17), 1365 (1), 1452 (34, br, d), 1464 (34), 2649 (0), 2719 (5), 2759 (5), 2852 (30), 2872 (180), 2908 (100, ba), 2931 (100, ba), 2961 (140).

EVALUATION OF RESULTS

Special attention is merited by the problem of the structure of the sterolsomers of 1,2,4-trimethylcyclopentane, 1,4-dimethyl-2-ethylcyclopentane and 1-methyl-3-ethylcyclopentane which we synthesized. All three possible isomers of 1,2,4-trimethylcyclopentane have been prepared previously [7]. The preparation had the constants:

B.p., °C (760 mm)	n_D^{20}	d_4^{20}
109,28	1,41057	0,74727
116,73	1,4185	0,76345
118	1,422	0,766

In conformity with the Auwers-Skita law, the hydrocarbon with the lowest b.p. was assigned the cis,trans,cis-structure, the next one the cis,cis,trans-structure, and the highest boiling hydrocarbon the cis,cis,cis-structure.

In a recent paper [9] Chiurdoglu and coworkers described the preparation of these three stereoisomers and their Raman spectra, but they deviated from the paper cited above in assigning a different spatial distribution of the side chains to these stereoisomers. Thus, they regard the lowest boiling isomer as the cis,cis,cis-form and the remaining two as trans-forms. It was stated in the paper that proof of this would be published later but the promised

* The previously described [4] spectrum of trans-1,4-dimethylcyclohexane was obtained with a less pure preparation of this hydrocarbon.

** The previously described [1] spectrum of n-octane was obtained with a less pure preparation of this hydrocarbon. The specimen used in the present investigation was synthesized by T. F. Bulanova.

*** The previously described [1] spectrum of 2,5-dimethylhexane was obtained with a very impure preparation of this hydrocarbon.

paper has not yet appeared.

We obtained two stereoisomers of 1,2,4-trimethylcyclopentane to which we attributed the following structures on the basis of the Auwers-Skita law: cis,trans,cis- with b.p. 109.2° (760 mm) and cis,cis,trans- with b.p. 116.8° (760 mm). Comparison of the constants and Raman spectra of our preparation of cis,cis,trans-1,2,4-trimethylcyclopentane with the spectra of Chiurdoglu's preparation shows that our preparation does not contain any appreciable amount of the higher boiling isomer (cis,cis,cis-form). Actually the spectrum of our preparation is lacking in the frequency of 865 cm^{-1}, with intensity 2 in the visual scale, which is characteristic (according to the data of the Belgian investigators) of the higher boiling isomer. Some other frequencies characteristic of the latter isomer, but less intense are also absent from the spectrum of our preparation.

It should be noted that the spectrum of our preparation contains the intensive frequency 761 cm^{-1} which, according to Chiurdoglu's data, is present in the cis,cis,cis-form but absent from the cis,cis,trans-form. We may assume, however, that this frequency occurs in the spectra of all three stereoisomers and was not detected by the Belgian investigators in the case of the cis,cis,trans-form due to the low resolving power of their spectrograph. Indeed for the latter isomer they observed a broad band at 751 cm^{-1} whereas we detected two closely located frequencies at 748 and 761 cm^{-1} of which the first was broad.

The data at our disposal for the Raman spectra of the stereoisomers of 1,2,4-trimethylcyclopentane enable us to draw conclusions about the spatial arrangement of the side chains in the two stereoisomers of 1,4-dimethyl-2-ethylcyclopentane which we separated and which may even exist in four forms. The repeated presence of characteristic frequencies in molecules of similar structure but with different chain lengths is a well-established fact [3, 4, 5, 6, 10]. It is known that in homologs of cyclopentane and benzene with one side chain as well as with two side chains, a series of closely repeating frequencies is observed. In Tables 1 and 2 are set forth as an example the principal frequencies (in cm^{-1}) and intensities of molecules of analogous structure but with different side chains. This observation has great practical significance; it sometimes permits the utilization of characteristic frequencies in the solution of specific problems of analysis and structure.

TABLE 1

m-Xylene	1-Methyl-3-ethylbenzene
539 (230)	530 (85)
726 (440)	721 (210)
1000 (540)	1002 (420)

TABLE 2

p-Xylene	1-Methyl-4-ethylbenzene
459 (200)	462 (20)
810 (110)	807 (140)
829 (410)	826 (140)
1205 (330)	1202 (160)

As we know, however, the concept of characteristic frequencies must not be unduly simplified and the occurrence of similar or repetitive frequencies must by no means be always regarded as a trustworthy criterion of group structure. A specific confirmatory indication of an empirical character in this connection is the reproducibility not only of the frequency but also of other characteristics of the investigated lines (intensity, polarization and width). The most trustworthy criterion of the suitability of empirical group indications is the development of theoretical methods of calculation of the vibrations of complex molecules which, aided by parameters determined from the spectra of a series of compounds, enable more or less detailed conclusions to be drawn about the spectra of more complex compounds. Such methods of calculation have been developed in the case of paraffins but are unfortunately lacking for other types of compounds, and we were compelled to make cautious use of purely empirical features. The reliability of the latter certainly increases with the accumulation of experimental material. In some cases, however, even relatively limited data may be turned to good account.

In this investigation the above-mentioned spectroscopic criterion was used for elucidation of the structure of the stereoisomers of 1,4-dimethyl-2-ethylcyclopentane and 1-methyl-3-ethylcyclopentane which we prepared, a problem that would have been extraordinarily difficult to solve by purely chemical methods. The structures were established by comparing the Raman spectra of our hydrocarbons with the spectra of hydrocarbons of similar structure, the spatial arrangement of whose side chains had been previously determined from chemical data. In Table 3 are given the frequencies and intensities of the principal lines of the trialkylcyclopentanes which were studied.

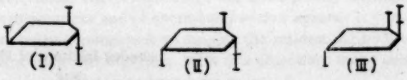
A comparison of the frequencies set forth in Table 3 clearly shows the resemblance between the spectrum of cis,trans,cis-1,2,4-trimethylcyclopentane and that of the lower boiling isomer of 1,4-dimethyl-2-ethylcyclopentane. The spectrum of cis,cis,trans-1,2,4-trimethylcyclopentane is likewise very similar to that of the higher

TABLE 3

Cis,trans,cis-1,2,4-trimethylcyclopentane	1,4-Dimethyl-2-ethylcyclopentane, isomer with b.p. 136.5°	Cis,cis,trans-1,2,4-trimethylcyclopentane	1,4-Dimethyl-2-ethylcyclopentane, isomer with b.p. 143.2°
422 (5)	420 (5)	498 (14)	501 (2)
490 (15)	483 (5)	520 (9)	516 (4)
529 (7)	524 (3)	748 (17)	745 (5)
	746 (2)	761 (20)	761 (10)
769 (44)	772 (7)	854 (6)	855 (6)
811 (8)	819 (4)		

boiling isomer of 1,4-dimethyl-2-ethylcyclopentane. In both cases the replacement of the methyl group by ethyl does not lead to a substantial change of frequencies; changes are only observed in the intensities, which in these cases diminish appreciably.

Consequently the lower boiling isomer evidently possesses the structure of cis,cis,trans-1,4-dimethyl-2-ethylcyclopentane (I). The spectrum of this hydrocarbon, however, contains the frequency of 746 cm^{-1} which has no analog in the spectrum of cis,cis,trans-1,2,4-trimethylcyclopentane. It is very probable that this frequency belongs to the spectrum of cis,trans,trans-1,4-dimethyl-2-ethylcyclopentane (II) which is bound to have a boiling point very close to that of the cis,cis,trans-form and which we were probably unable to separate from the latter.



By the same reasoning the higher boiling isomer must be cis,trans,cis-1,4-dimethyl-2-ethylcyclopentane (III). It should be noted that the spectrum of our preparation does not contain any frequency similar to the frequency of 865 cm^{-1} which, as mentioned above, is characteristic of cis,cis,cis-1,2,4-trimethylcyclopentane. We may therefore conclude that in the case of 1,4-dimethyl-2-ethylcyclopentane as well as of 1,2,4-trimethylcyclopentane, the cis,cis,cis-form is not present in our preparation.

A comparison carried out in a similar manner of the spectrum of our preparation of 1-methyl-3-ethylcyclopentane with the spectral data in the literature for the cis- and trans-forms of 1,3-dimethylcyclopentane, also a comparison with our data for the mixture of stereoisomers of this hydrocarbon and for the mixture of cis-trans-forms of 1-methyl-3-n-propylcyclopentane previously obtained by us, enable the trans-form to be assigned to our preparation. The hydrocarbons 1,3-dimethylcyclopentane and 1-methyl-3-n-propylcyclopentane, respectively the cis- and trans-forms, have the following characteristic frequencies: first hydrocarbon – 803 and 828 cm^{-1}; second – 817 and 832 cm^{-1}. The 1-methyl-3-ethylcyclopentane that we investigated has the frequency 837 cm^{-1} which is close to the frequency characterizing the trans-form.

In conclusion we take this opportunity of conveying our sincere gratitude to G. S. Landsberg for valuable advice in the course of the work.

SUMMARY

1. Details of the Raman spectra are given of seven cyclopentane and cyclohexane hydrocarbons, including two hydrocarbons synthesized for the first time. All the intensities of the Raman frequencies are set forth in a uniform scale.

2. The spectroscopic data served as a basis for evaluation of the problem of the spatial arrangement of the side chains in 1-methyl-3-ethylcyclopentane and in the stereoisomers, synthesized for the first time, of 1,4-dimethyl-2-ethylcyclopentane.

3. New data are presented for the Raman spectra of three hydrocarbons for which data had previously been obtained on the basis of less pure specimens.

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Received August 30, 1953

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HIGH MOLECULAR COMPOUNDS OF PETROLEUM

COMMUNICATION 1. APPLICATION OF COLOR PHOTOGRAPHY TO THE CHARACTERIZATION OF LUMINESCENCE

S. R. Sergienko, Yu. A. Bedov and M. P. Teterina

Chemical and physical advances have made possible the investigation of complex organic compounds containing hundreds and thousands of atoms in their molecules. The chemistry of high-molecular compounds, stemming from organic chemistry, has enabled closer investigation of the chemical properties and structure of numerous natural substances.

The chemistry of high-molecular compounds has developed a number of new methods of resolution and examination of the giant molecules of complex organic compounds. In these studies a particularly important part has been played by physical methods. The usual effect of reactive chemicals and high temperatures upon high-molecular compounds is to change their composition, structure and molecular weight. This is particularly true of high-molecular compounds containing nitrogen, sulfur and oxygen which are consequently distinguished by exceptional instability under the influence of high temperatures and of chemically active agents. It is particularly important when studying such unstable high-molecular organic compounds to employ the mildest methods in order to exclude chemical transformations during the very process of investigation. With this objective, many purely physical methods of resolution and investigation of high-molecular substances have been proposed.

Up to recently petroleum had not been subjected to examination by the special methods developed by the chemistry of high-molecular compounds. This is because industrial use has been made of the low-molecular and middle fractions of petroleum, whereas the heavier portion of petroleum, in which are concentrated the high-molecular hydrocarbon and asphaltene-resin constituents, have remained waste products of the industry. In the early stages of its development, the petroleum processing industry repeated the historical course of organic chemistry: in both cases, that which could not be distilled without decomposition was called " resin" and was rejected as undeserving of the attention of the chemist. These high-molecular "resinous" organic compounds have actually now become the objects of investigation of the chemistry of high-molecular compounds.

Today one of the most important scientific and technological problems of petroleum processing is that of the complete, i.e. residueless, processing and utilization of petroleum as a chemical raw material. Consequently the high-molecular, resinous portion of petroleum, amounting to 10-50% of the total, depending on the source, must be included in the processing scheme. In order to use this complex chemical raw material in industry to the best advantage, a detailed study is necessary of its chemical composition, structure and principal reactions. That is why the chemistry of high-molecular compounds of petroleum has now acquired such wide importance.

Unlike such high-molecular compounds as rubber, cellulose, etc., the high-molecular compounds of petroleum are characterized by relatively low molecular weights (500-5000) and by the absence of a fundamental structural unit whose polymerization could lead to a chain-like giant molecule containing regularly repeated structural links. In spite of their relatively low molecular weight, the high-molecular compounds of petroleum are distinguished by extremely low stability to chemical and thermal action. This behavior must be taken into consideration when separating the complex mixture of high-molecular compounds of petroleum.

The method of adsorption chromatography of Tsvet [1] was proposed a long time ago for the separation of the resin-asphaltenic substances of petroleum from the hydrocarbons for the purpose of their quantitative determination. Utilization of silica gel as an adsorbent for the resins has acquired great popularity, ever since the work of Gurvich [2] and Sakhanov and Vasilyev [3], both for analytical and processing purposes in the petroleum industry. Total separation of the resins of petroleum products with the help of an adsorbent such as silica gel has been effected with full success.

The study of the composition and chemical nature of the main components of the high-molecular substances of petroleum necessitates in the first place their resolution into narrower fractions. For this purpose advantage is

taken of the differing solubility and adsorbability of the constituents of the resin-asphaltene portion of petroleum. Chernozhukov and Luzhetsky [4] used phenol as the selective solvent for separation of the resins. Tilyupo and Chernozhukov [5] effected resolution of petroleum resins by adsorptive chromatography on silica gel followed by fractional desorption of the resins from the silica gel with organic solvents and by further resolution of the obtained fractions into phenol-soluble and phenol-insoluble substances.

EXPERIMENTAL

In our studies of high-molecular compounds of petroleum we likewise made use of a combined scheme of separation of hydrocarbons and resins based on the differing absorbability on silica gel of the individual components of this complex mixture of organic compounds and also on their differing extractability by organic solvents. The general scheme of separation, as modified by us (Fig. 1), permitted first of all a sufficiently complete separation from the mixture of the hydrocarbon portion, and then a closer fractionation of the resin adsorbed onto silica gel with the help of extracting liquids of differing polarities and of a selectively acting solvent (phenol). The application of adsorption analysis to the hydrocarbon portion permitted the characterization of its group composition [6].

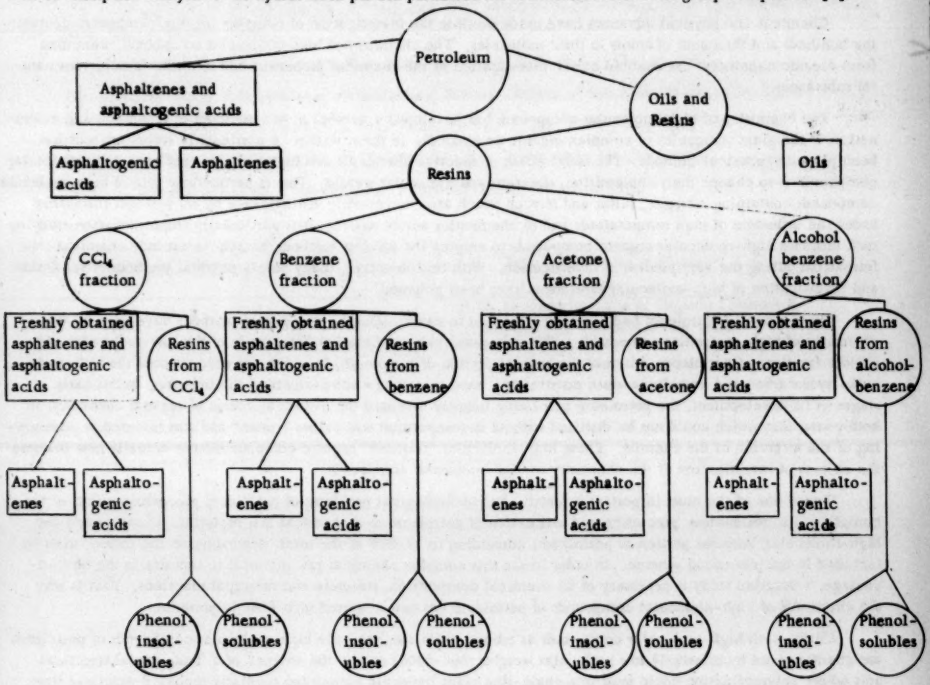

Fig. 1. General scheme for resolution of the resin-asphaltenic portion of petroleum.

We have already described in detail [7] the procedure for resolution of the high-molecular portion of petroleum. It involves subjecting the petroleum or petroleum product to investigation after preliminary freeing from asphaltenes by 40-fold dilution with isopentane and filtering through a silica gel column (fraction of silica gel retained on 32 meshes-to-the-inch screens). After washing the hydrocarbon portion with ligroine, the resins adsorbed on the silica gel were fractionally extracted from the silica gel by successive treatment with a series of organic solvents of gradually increasing polarity (carbon tetrachloride, benzene, acetone, 1:1 alcohol/benzene mixture). The obtained resin fractions were later freed from solvents and subjected to treatment with phenol for separation into phenol-soluble and pheol-insoluble portions. The resin fractions obtained by this procedure were characterized by determinations of molecular weight, acidity, content of unsaturateds, chemical composition and type of luminescence.

Luminescence Analysis

Although the luminescence method of characterization of substances also suffers from the drawback that the luminescence is insufficiently specific and cannot be such a decisive characteristic of substances as the adsorption spectra or Raman spectra, it nevertheless proves to be suitable and useful for observation of the qualitative changes taking place in a substance, particularly in the case of petroleum resins, due to various chemical and physical interactions (oxidation, hydrogenation, resolution into fractions, etc.). With consumption of very little material, luminescence analysis permits the observation of qualitative changes in a substance with the help of the change in the character of the luminescent radiation.

For the observation of luminescence we made use of the method of paper chromatography. Strips of filter paper were first extracted in a Soxhlet apparatus with alcohol-benzene mixture for 6 hours to eliminate luminescing impurities. The so-prepared filter paper strips of width 1 cm and length 15-20 cm were suspended over small beakers into each of which was poured 5 ml of 0.001% solution of the resin sample in 1:1 alcohol-benzene. The filter paper strips were suspended in such a manner that they did not touch the walls of the beaker and were immersed in the solution to the bottom. The samples were left in this state for 12-14 hours (usually overnight). During this period the surplus solvent evaporated from the beaker and also the solvent imbibed by the paper. The dry samples were inspected in the light of a PRK-2 quartz lamp filtered through a FS-4 light filter transmitting only blue and ultraviolet rays.

Our observations of the luminescence revealed a number of characteristics of the samples of resins which had been subjected to various treatments. However, up to now attempts to objectively represent the observed picture of the luminescence or to describe it have proved unsuccessful. Drawings ot the luminescence picture, apart from the enormous labor and the special abilities that they demand from the artist, suffer from subjective transfer, since they depend on the color perception of the investigator. Each time that it is necessary for a communication about an observed luminescence picture to be sent to a printer or elsewhere, it is necessary either to prepare the appropriate specimens and start up the luminescence lamp or to limit oneself to a description, in which event the picture loses all its objectivity and significance. We therefore undertook experiments to obtain a permanent record of the luminescence of the paper chromatogram of the resin solutions by color photography.

Photographs were taken with a "Kiev" camera on DS-1 color negative film supplied by a Russian manufacturer. The set-up for the photography is shown in Fig. 2.

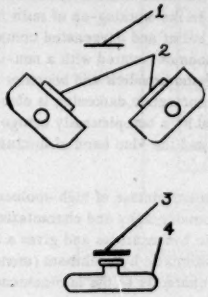

Fig. 2. Set-up for luminescence photography: 1) screen with samples; 2) PRK-2 lamp with FS-4 filter; 3) lead glass; 4) "Kiev" camera

All the color materials were processed by the usual methods used in color photography. The specimens were irradiated from two sides with PRK-2 quartz lamps through FS-4 light filters. For absorption of the ultraviolet rays, reflected from the lens of the camera and causing appearance of a blue tone on the photograph, in front of the lens of the camera was placed an ultraviolet absorption filter. For this purpose we tried out a series of color filters. We used a color filter film, made by the Agfa firm, and liquid color filters. In addition, as color filters we used lead glass 12 mm thick. The liquid color filter was constructed in the following manner: a cell 25 mm thick with parallel walls of ordinary glass, open at the top, was filled with one of the substances. Care was taken during filling to ensure that air bubbles did not adhere to the sides and did not distort the photograph. As the filling liquids we used distilled water, saturated solution of common salt and carbon bisulfide which had a fairly high absorption in the blue and near ultraviolet region of the spectrum. By the same token (absorption in the blue and near ultraviolet region of the spectrum), Agfa light filters [8] were selected whose absorption curves are shown in Fig. 3.

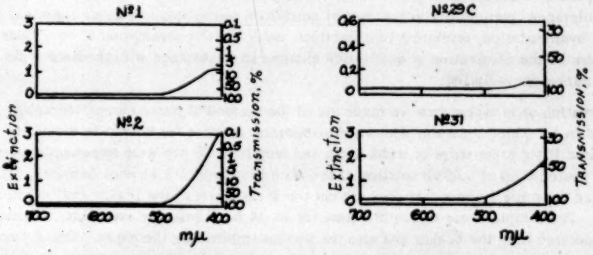

Fig. 3. Absorption curves of Agfa light filters.

In Figures 4 and 5 are shown photographs of the luminescence of specimens of resins taken with various light filters. Prints were made without the use of correcting filters during printing. Examination of the photographs shows that the Agfa No. 31 filter does not completely remove the blue background and considerably reduces the intensity of the yellow luminescence band. Agfa No. 1 filter and the liquid filters containing sodium chloride solution and distilled water gave a similar result and therefore the corresponding prints are not reproduced. Agfa No. 29 filter gives relatively good light transmission of the colored zones but also lowers the intensity of the yellow luminescence. The most successful results were got when using Agfa No. 2 filter, the liquid carbon disulfide color filter and lead glass. Since of these the most readily available and the simplest in use was lead glass, and since the quality of the pictures obtained with the other filters was not superior, we decided to use lead glass in all the later work. Photographs of the luminescence of various specimens of resins are reproduced in Figs. 6 and 7. Inspection of these photographs shows that the method of observation of color photographs of luminescence enables differentiation between specimens of resins containing asphaltenes and those not containing asphaltenes. In the working-up of resin fractions with phenol, leading to enrichment of the phenol-soluble portion with aromatic, sulfur and oxygenated compounds, the yellow band of luminescence for the phenol-soluble resins contracts and becomes covered with a non-luminescing layer. Conversely, for the pheno-insoluble resins, the yellow luminescent band broadens and becomes more intense. In the specimens of oxygenated resins, on the color photographs of the luminescence, darkening is observed of nearly the whole of the luminescent region; the light-yellow tones are replaced by a conspicuously orange color, in the case of hydrogenated resins however, the color becomes more light-yellow and the blue band of luminescence characteristic of polycyclic hydrocarbons is developed.

Of very great interest are the color photographs of the luminescent picture of high-molecular hydrocarbons "light" oils and "dark" oils isolated with the help of adsorption chromatography and characterized by us previously. The so-called light oil contains predominantly naphthenic-paraffinic hydrocarbons and gives a light-blue luminescence. The "dark" oils, however, consisting almost completely of aromatic hydrocarbons (mono- and bicyclic) with a small admixture of resins, give a yellow luminescence similar in character to the luminescence of the resins.

To minimize the risk of image distortion during the positive process, we made attempts to take photographs on reversal film. Due, however, to the difficult availability of the film and the possibility of obtaining only one picture which could not be duplicated, we had to abandon this method although it gave good results. Attempts to reverse negative film and photographic paper have not yet given satisfactory results.

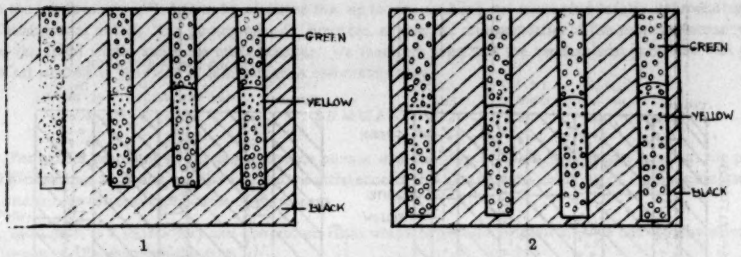

Fig. 4. Photographs* of luminescence of specimens of resins, taken with various Agfa filters:
1 – Agfa No. 31. 2 – Agfa No. 29.

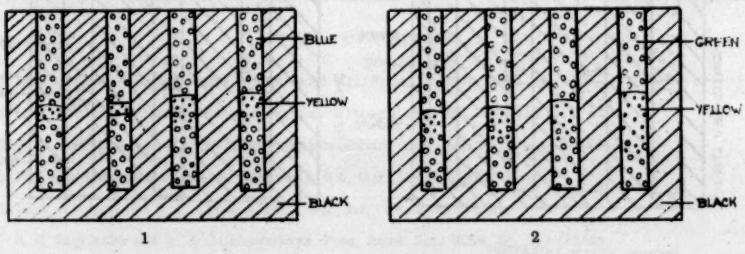

Fig. 5. Photographs* of luminescence of samples taken with various filters:
1 – CS2 filter. 2 – Lead glass filter.

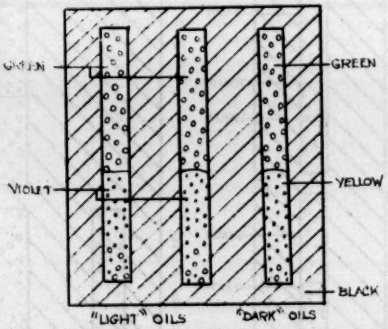

Fig. 7. Photographs* of luminescence of various samples of high-molecular hydrocarbons of Romashk petroleum.

* The color photographs accompanying this paper in the original could not be reproduced in color by the process used to publish this translation. Reproduction in black-and-white would have completely distorted the relative size of areas in the spectra. We have therefore interpreted these photographs in this manner, so that the relative areas of luminescence referred to in the text might be apparent. Publisher.

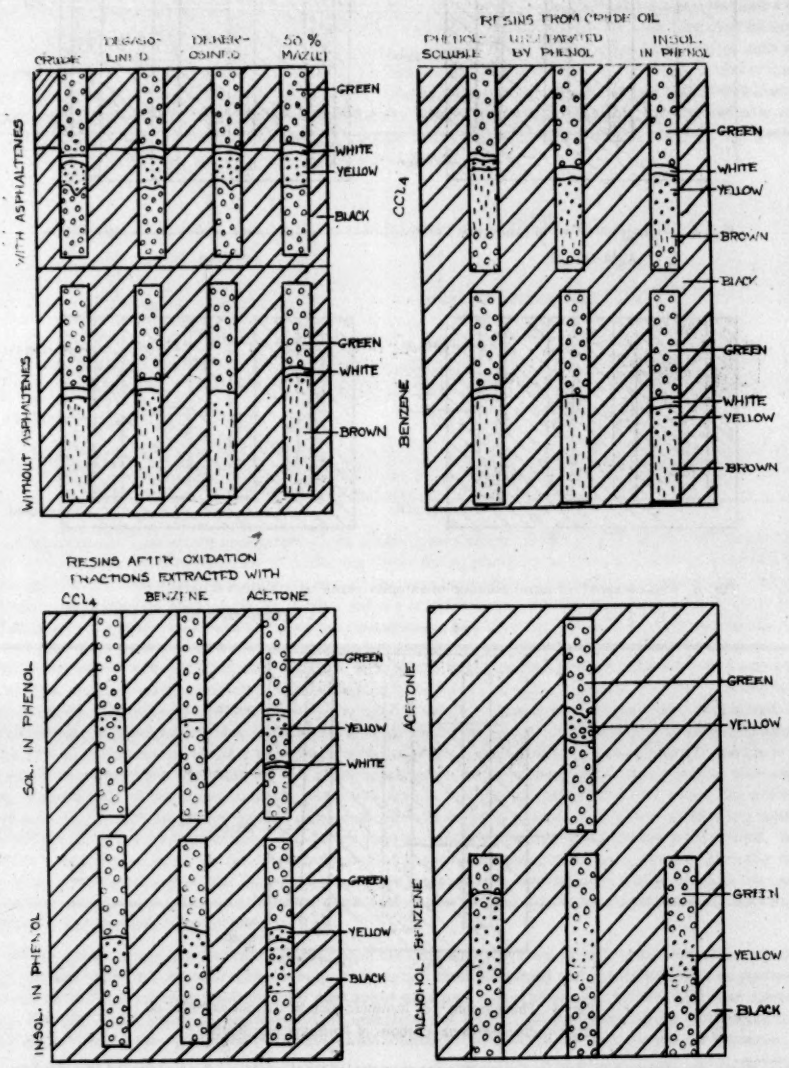

Fig. 6. Photographs of luminescent radiation of various samples of Smolromashk: oil.

From the results set forth above we see that the application of color photography to the permanent recording of luminescence pictures opens up the possibility of eliminating the influence of the subjective judgement of the observer on the luminescence. It has to be admitted that up to now we have not succeeded infully reproducing the original luminescent colors. The photographs do, however, enable the representation of the relative intensity of the radiation, the zonal widths and some other features. We therefore hope that the method here published will prove useful for all workers in the field of luminescence chromatography.

SUMMARY

1. Permanent recording of the luminescence picture with the help of color photography provides the possibility of fully objective assessment of the qualitative difference in the luminescent radiation of various components of the high-molecular resinous compounds of petroleum.

2. Lead glass is a satisfactory and convenient filter which retains the ultraviolet rays and thereby eliminates their influence on the photographic film.

3. The supplementing by color photography of luminescence analysis is an objective method for qualitative evaluation of the chemical changes in the components of the high-molecular resins of petroleums.

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Received September 20,1953

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SYNTHESIS AND PHYSICAL AND CHEMICAL PROPERTIES OF VINYLETHYNYLSILANES

A. D. Petrov, S. I. Sadykhzade and Yu. P. Egorov

The dimer of acetylene – 1-buten-3-yne – is used as a raw material for the production of the synthetic rubber known as chloroprene; it also condenses with ketones to form readily polymerizable carbinols applicable as glues.

The organomagnesium compound of 1-buten-3-yne (readily condensable with aldehydes and ketones) is not capable, however, of undergoing the Grignard-Würtz condensation either with primary, secondary or even tertiary alkyl halides. Exceptions, as shown by Carothers and Nieuwland, are such active halides as triphenylchloromethane [1] and allyl bromide [2]. The synthesis of saturated and aromatic tetrasubstituted silanes is effected, as we know, on the basis of $SiCl_4$ and its mono-, di- and trisubstituted derivatives whose halogen atoms are substituted with facility by both aliphatic and aromatic radicals. We investigated the condensation of 1-buten-3-ynyl magnesium halide with such active halides as alkyl- and arylhalosilanes. It was established that this reagent indeed interacts with high yields with R_3SiCl, R_2SiCl_2 and $RSiCl_3$ and even with $SiCl_4$ but does not condense with primary or even with α- and β-secondary silicon halides of the type of:

$$\gtrless Si-CH_2 \cdot X, \quad \gtrless Si-\underset{\displaystyle CH_3}{\underset{|}{CH}}-X, \quad \gtrless Si-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-X$$

The so-prepared vinylethynylsilanes were readily polymerized. We thus found a route to silicohydrocarbons of the enyne type with similar properties to the oxygen-containing derivatives of 1-buten-3-yne or the so-called carbinols.

The first reference to vinylethynylsilanes, specifically to 1-triethylsilyl-3-methyl-3-penten-1-yne, was made by the English physicist Bowden [3]. Petrov and Sadykhzade reported [4] the synthesis by condensation of $MgBr-C\equiv C-CH=CH_2$ with R_3SiCl – of four trialkylvinylethynylsilanes, while by condensation with R_2SiCl_2 they obtained three dialkyldivinylethynylsilanes. The physical properties of these seven compounds are set forth in Table 1.

In connection with the chemical properties of these silanes, Kucherov observed the inability to be hydrogenated of the triple bond in the α-position to the silicon (in more drastic conditions there is rapid decomposition of the ketone with the carbonyl group in the β-position as formed); later he noted the addition of both two and four atoms of bromine followed by cleavage of HBr in the latter case. These data as well as the study of the synthesis and properties of silicoacetylenic hydrocarbons of Frisch and Joung [5] permit us to conclude that in the case of vinylethynylsilanes the bromine only adds on at the triple bond. It was also established that vinylethynylsilanes are easily hydrogenated over palladium oxide both fully to butylsilanes and selectively with absorption of two or four atoms of hydrogen. In the former case the main product of hydrogenation was trialkylbutadienylsilane, as was confirmed by the formation with maleic anhydride of an adduct with m.p. 132°. When four hydrogen atoms were absorbed the main product was trialkyl-2-butenesilane as was confirmed by the examination of its Raman spectrum (see below).

We also obtained a series of aliphatic-aromatic vinylethynylsilanes; their physical properties are set forth in Table 2. Concerning their chemical properties, interest is attached to their polymerization tendency which is lower than that of trialkylvinylethynylsilanes and especially great in the case of dimethyl-p-tolyl-vinylethynylsilane. It is also interesting to note that triphenylchlorosilane, in the usual conditions at any rate, (as used by us for condensations of all three substituted halosilanes with $MgBrC\equiv C-CH=CH_2$ at relatively low temperatures below 100°), failed to condense. This fact illustrates the known contrast in properties between $(C_6H_5)_3 \cdot CCl$ (I) and $(C_6H_5)_3 \cdot SiCl$ (II), and between $(CH_3)_3 CCl$ (III) and $(CH_3)_3 \cdot SiCl$ (IV). The first halide condenses with $MgBrC\equiv C-CH=CH_2$, the second does not condense [and the sole product of reaction is $(C_6H_5)_3 SiOH$ with m.p. 151°], the third does not condense, and the fourth condenses with high yield. These facts illustrate the wide diversity of properties of the tertiary halides and of the corresponding silicohalides formed from them by the Grignard-Würtz reaction.

TABLE 1

Properties of Trialkylmonovinylethynylsilanes and Dialkyldivinylethynylsilanes

Substance	B.p. in °C (in mm mercury)	d_4^{20}	n_D^{20}	MR found	MR calculated*	Yield %	Found (%) C	Found (%) H	Found (%) Si	Calculated (%) C	Calculated (%) H	Calculated (%) Si
Trialkylmonovinylethynylsilanes												
Trimethylvinylethynylsilane $(CH_3)_3Si-C\equiv C-CH=CH_2$	52-53 (80)	0.7714	1.4510	43.35	42.09 43.39	55.0	67.04	10.12	–	67.60	9.81	–
Triethylvinylethynylsilane $(C_2H_5)_3Si-C\equiv C-CH=CH_2$	74-76 (20)	0.8145	1.4695	56.33	55.98 57.28	52.7	72.41	11.40	15.91	72.22	10.90	16.84
Tripropylvinylethynylsilane $(C_3H_7)_3Si-C\equiv C-CH=CH_2$	87-89 (7)	0.8173	1.4700	71.13	69.87 71.17	51.6	74.81	11.70	12.85	74.92	11.61	13.46
Tributylvinylethynylsilane $(C_4H_9)_3Si-C\equiv C-CH=CH_2$	108-110 (8)	0.8201	1.4700	85.18	83.76 85.06	53.1	–	–	11.82	–	–	11.26
Dialkyldivinylethynylsilanes												
Dimethyldivinylethynylsilane $(CH_3)_2Si-(C\equiv C-CH=CH_2)_2$	67-68 (9)	0.8495	1.5108	56.49	53.90 56.50	57.2	74.58	8.08	17.	74.96	7.96	17.50
Diethyldivinylethynylsilane $(C_2H_5)_2Si-(C\equiv C-CH=CH_2)_2$	84-86 (8)	0.8556	1.5140	66.22	63.16 65.76	38.4	76.96	8.7	–	76.47	8.52	–
Dipropyldivinylethynylsilane $(C_3H_7)_2Si-(C\equiv C-CH=CH_2)_2$	84-85 (5)	0.8561	1.5145	76.12	72.42 75.02	36.4	77.70	9.11	13.28	77.67	9.24	12.94

* The first of the pair of values was calculated on the basis of [11] the refraction of the Si–C bond was assumed to be equal to 2.5 just as for the alkylsilanes. The lower value corresponds to the mean value of the Si–C bond, assumed to be equal to 3.8 when C is attached to the $-C\equiv C-\underset{H}{\overset{}{C}}-\underset{H_2}{\overset{}{C}}$ radical.

TABLE 2 Properties of Dimethylarylvinylethynylsilanes

Substance	B.p. in °C (p in mm Hg)	d_4^{20}	n_D^{20}	Yield (%)	Found % C	Found % H	Found % Si	Calculated % C	Calculated % H	Calculated % Si	MR Found	MR Calculated
Dimethylphenylvinylethynylsilane $(CH_3)_2C_6H_5Si-C\equiv C-CH=CH_2$	83-84 (6.5)	0.9229	1.5391	69.2	77.50	7.38	14.80	77.35	7.52	15.08	63.25	63.06
Dimethylbenzylvinylethynylsilane $(CH_3)_2(CH_2C_6H_5)Si-C\equiv C-CH=CH_2$	111-112 (11)	0.9185	1.5391	60.6	78.15	7.95	13.33	77.91	7.99	14.00	68.33	68.69
Dimethyltolylvinylethynylsilane $(CH_3)_2(CH_3C_6H_4)Si-C\equiv C-CH=CH_2$	112-113.5 (10)	0.9147	1.5368	69.6	77.89	7.93	14.20	77.91	7.99	14.00	68.37	68.69
Dimethyl-α-naphthylvinylethynylsilane $(CH_3)_2\alpha\text{-}C_{10}H_7Si-C\equiv C-CH=CH_2$	146-147.5 (6)	1.0116	1.6029	45.4	80.84	6.97	10.87	81.27	6.87	11.77	80.25	79.56

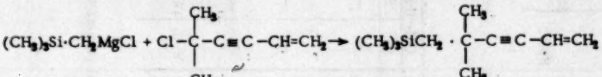
MR is calculated on the basis of new data for the Si−C bond when in the case of $C\equiv C-\underset{H}{\overset{|}{C}}=\underset{H_2}{\overset{|}{C}}$ it is equal to 3.8

TABLE 3 Properties of Halogeno- and Alkoxy Derivatives of Vinylethynylsilanes

Substance	B.p. in °C (p in mm Hg)	d_4^{20}	n_D^{20}	MR Found	MR Calc.	Yield (%)	Found % C	Found % H	Found % S	Found % Cl	Calculated % C	Calculated % H	Calculated % S	Calculated % Cl
Methylvinylethynyldichlorosilane $CH_3(CH_2=CH-C\equiv C)SiCl_2$	49-50 (24)	1.0871	1.4760	42.83	42.65	29.7	–	–	–	43.10	–	–	–	43.03
Methyldivinylethynylmonochlorosilane $CH_3(CH_2=CH-C\equiv C)_2SiCl$	88-89 (12)	0.9471	1.5224				–	–	–	16.92	–	–	–	19.65
Vinylethynyltrichlorosilane* $CH_2=CH-C\equiv C\cdot SiCl_3$	67-69 (60)					22.3	–	–	–	56.96	–	–	–	57.42
Vinylethynyltriethoxysilane $(CH_2=CH-C\equiv C)Si(OC_2H_5)_3$	78-79 (7)	0.9407	1.4352	59.47	59.56	34.0	56.84	8.15	11.56	–	56.14	8.45	13.0	–

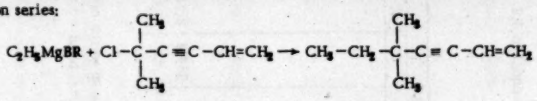
* This compound fumes in the air and is instantaneously hydrolyzed by atmospheric moisture, due to which circumstance its physical properties could not be determined. The MR was calculated on the basis of new data for the magnitudes of the Si−C bond = 3.8, in the case of the $\equiv Si-C\equiv C-\underset{H}{\overset{|}{C}}=\underset{H_2}{\overset{|}{C}}$ radical.

Attempts to carry out the condensation of $MgBrC{\equiv}C-CH{=}CH_2$ with the primary silicohalide, siliconeopentyl chloride $(CH_3)_3Si \cdot CH_2 \cdot Cl$, proved unsuccessful and we were unable to introduce a triple bond in the β-position to the silicon. But the condensation of the Grignard reagent from this silicohalide with dimethylvinylethynylchloromethane was successful and gave an enynic silicohydrocarbon with a triple bond in the γ-position to the silicon-dimethylsiliconeopentyl-vinylethynylmethane,

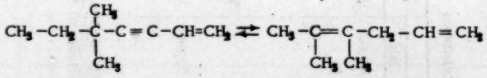


The Raman spectrum was plotted of the silicohydrocarbon [b.p. 67–69° (6 mm); d_4^{20} 0.8088, n_D^{20} 1.4725. Found %: C 73.40; H 11.01; Si 14.7. Calculated %: C 73.37; H 11.18; Si 15.4]. The following intense frequencies were found: 695 (3), 1290 (5), 1610 (5), 2217 (6), 1407 (3), 1466 (6). Attention should be drawn to the considerable increase of the frequency of C ≡ C to 2217 cm^{-1}, by comparison with the value of 2158 cm^{-1} when the vinylethynyl group is linked directly with Si. The low yield of the silicohydrocarbon prevented its more detailed study.

Bearing in mind that according to the data of Pudovik and Mukhamedova [6] an analogous reaction in the hydrocarbon series:



took place with partial isomerization of the acetylene linkage



it is highly probable that in our case a partial isomerization of this type took place.

Since it appeared to us that the vinylethynyl radical, like the vinyl and allyl radicals, is of interest not only in purely hydrocarbon chains of polymers but also in siloxane chains, we synthesized methylvinylethynyldichlorosilane, methyldivinylethynylmonochlorosilane, vinylethynyltrichlorosilane and triethoxyvinylethynylsilane. The physical properties of these compounds are set forth in Table 3.

Data for the Raman spectra and infrared absorption spectra of the vinylethynylsilanes which we synthesized are set forth below and plotted in the diagrams.

1. Triethylvinylethynylsilane cm^{-1}: 301 (5 ba), 570 (25), 611 (25), 674 (10), 728 (14 br), 972 (12 br), 922 (10), 1014 (12 br), 1110 (15), 1232 (25 br), 1290 (25), 1353 (3), 1392 (1), 1410 (45), 1460 (24), 1595 (38), 1611 (70), 2154 (210), 2217 (15), 2880 (90), 2908 (45), 2939 (40), 2961 (45), 3015 (42), 3105 (23).

2. Methylethylvinylethynylsilane cm^{-1}: 300 (5 ba), 579 (30), 630 (30), 649 (22), 682 (8), 710 (8), 748 (18 br), 835 (9), 885 (2), 927 (10), 972 (7), 1014 (5), 1110 (20), 1233 (12), 1257 (8), 1290 (26), 1353 (6), 1410 (50), 1460 (8), 1595 (58), 1611 (58), 2145 (48), 2154 (250), 2217 (15), 2880 (25), 2908 (40 br), 2940 (10), 2965 (35), 3015 (45), 3104 (25).

3. Methyldivinylethynylsilane cm^{-1}: 300 (8), 580 (25), 602 (6), 685 (20 br), 742 (25), 761 (2), 835 (10), 884 (10), 925 (8), 961 (8), 1054 (2), 1110 (27), 1253 (10), 1290 (31), 1352 (5), 1410 (70), 1595 (85), 1611 (33), 2145 (45), 2156 (280), 2217 (22), 2872 (10), 2908 (25 br), 2961 (12), 2978 (30), 3012 (52), 3101 (30).

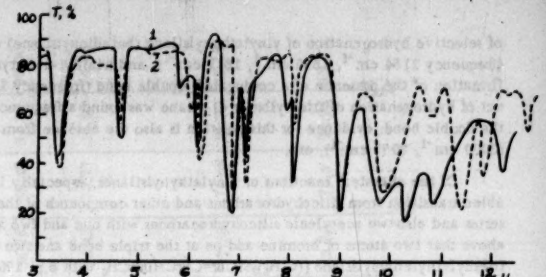
4. Triethoxyvinylethynylsilane cm^{-1}: 590 (12), 685 (3), 714 (16 br), 794 (8 br), 932 (10), 1043 (3), 1089 (10 br), 1110 (15 br), 1290 (21), 1352 (5), 1410 (32), 1448 (10), 1595 (67), 2154 (160), 2217 (10), 2867 (20 br), 2882 (30), 2930 (52), 2978 (44), 3014 (35), 3100 (20).

The Raman spectra were obtained with the ISP-51 apparatus, using the usual technique [6] for measurement of frequencies and intensities. The intensity of the 802 cm^{-1} frequency of cyclohexane was assumed to be 250 units. The measurements of the intensities were accurate to 15%, those of frequencies were accurate to ± 1 cm^{-1} for narrow lines and ± 3 cm^{-1} for broad or very weak lines. The infrared absorption spectra were obtained with an IKS spectrograph using a sodium chloride prism. The measurements of the bands at their minimum were accurate to ± 10 cm^{-1}. Examination of the spectra revealed a number of characteristic frequencies which are detailed in Table 4. The intensities of the frequencies are converted to the basis of identical numbers of molecules in the scattering volume.

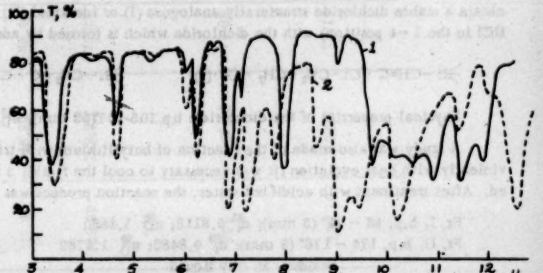
TABLE 4

Characteristic Frequencies of the $\equiv Si-C\equiv C-CH=CH_2$ Radical

Substance	Frequencies in cm^{-1}, intensities per mole								
$(C_2H_5)_2SiC\equiv C-CH=CH_2$	1110 (24)	1290 (40)	1353 (5)	1410 (73)	1595 (61)	1611 (112)	2154 (340)	2217 (24)	3015 (68)	3105 (37)
$(C_2H_5)(CH_3)Si-C\equiv C-CH=CH_2$	1110 (25)	1290 (32)	1357 (7)	1410 (62)	1595 (73)	1611 (73)	2154 (310)	2217 (19)	3015 (69)	3104 (3)
$CH_3HSi(C\equiv C-CH=CH_2)_2$	1110 (38)	1280 (42)	1352 (7)		1595 (115)	1611 (45)	2156 (380)	2217 (30)	3014 (70)	3101 (40)
$(C_2H_5O)_3Si-C\equiv C-CH=CH_2$	1110 (27)	1290 (38)	1352 (9)	1410 (58)	1595 (120)	–	2154 (290)	2217 (18)	3014 (63)	3100 (36)



1) $(C_2H_5)_2SiC\equiv C-\underset{H}{\underset{|}{C}}=CH_2$; 2) $CH_3Si(C\equiv C-\underset{H}{\underset{|}{C}}=CH_2)_2$



1) $(CH_3)(C_2H_5)SiC\equiv C-\underset{H}{\underset{|}{C}}=CH_2$; 2) $(C_2H_5O)_3SiC\equiv C-\underset{H}{\underset{|}{C}}=CH_2$

The frequencies set forth may serve as an analytical characteristic of the vinylethynyl radical. Attention may be drawn to the position of the frequencies of the C≡C linkage at 2154 cm^{-1} and 2217 cm^{-1} and of the C=C linkage at 1596 and 1611 cm^{-1}, to the valence vibrations in the $=CH_2$ group at 3015 and 3104 cm^{-1}, and to the deformation vibrations in the $-CH=CH_2$ group at 1290; 1353, and 1410 cm^{-1} [7,8]. A striking feature is the absence of characteristic regularities of intensities, evidently due to strong interaction of the electronic clouds at the frequencies of the triple and double conjugated linkages in opposition to the allylsilanes. Similar analytically characteristic bands in the infrared spectrum have the values of 4, 6, 6.0, 6.2, 6.9, and 9.0 μ.

This investigation enabled us to solve diverse problems of the determination of the structure of derivatives of vinylethynylsilanes. We give some examples. The addition of bromine to the triple bond of vinylethynylsilanes was confirmed by the infrared spectra, the absence from which of bands in the 4 μ region in association with the presence of a band at 6.15 μ being characteristic of the C=C bond.

The spectra of acetylenic hydrocarbons (evaluated below) invariably showed the frequency of the triple bond in the α-position to be 2175 cm^{-1}, which enabled the determination in the spectrum of the above-mentioned product

of selective hydrogenation of vinylethynylsilane (butadienylsilane) of contamination with both the starting material (frequency 2154 cm^{-1}, 1595 cm^{-1}, 1611 cm^{-1}), and trialkyl-1-butynesilane (frequency 2175 cm^{-1}); it also gave confirmation of the presence of a conjugated double bond (frequency 1625 cm^{-1}). In the spectrum of the second product of hydrogenation of triethylbuten-2-silane was found a frequency of 1656 cm^{-1}, which confirmed the position of the double bond; evidence for this position is also the absence from the spectrum of the frequencies of the $-CH_2$ group (3000 cm^{-1}, 3075 cm^{-1}), etc.

Of the chemical reactions of vinylethynylsilanes, especially interesting were the addition reactions which enabled transition from silicohydrocarbons and other compounds of the enynic series to compounds of the butadiene series and also two acetylenic silicohydrocarbons with one and two atoms of silicon. We have already mentioned above that two atoms of bromine add on at the triple bond and two atoms at the double bond. The tribromide of triethylvinylethynylsilane [$(C_2H_5)_3SiBr{=}CBrCHBr{=}CH_2$ with b.p. 170 – 172° (11 mm); n_D^{20} 1.5889 and d_4^{20} 1.5605] that we prepared proved to be very stable; it did not decompose when kept for many weeks and it slowly polymerized. The stability of the dibromide of vinylethynylsilane prompted us to attempt the addition of gaseous HCl to trimethylvinylethynylsilane at −70°. In these conditions the HCl does not rupture the Si−C linkage so that we were able to obtain a stable dichloride structurally analogous (I) or identical (II) (in the case of addition of a second molecule of HCl in the 1–4 position) with the dichloride which is formed by addition of two moles of HCl to 1-buten-3-yne:

$$\gtrless Si-CH{=}C\cdot Cl-CH_2-CH_2\cdot Cl \quad (I) \qquad \gtrless Si-CH_2-C\cdot Cl{=}CH-CH_2\cdot Cl, \quad (II)$$

Physical properties of the dichloride: b.p. 105-107 (52 mm); n_D^{20} 1.4738; d_4^{20} 1.0092.

A study was also made of the reaction of butyllithium with triethylvinylethynylsilane. The reaction proceeded violently with heat evolution (it was necessary to cool the flask); a bluish-green organometallic compound was formed. After treatment with acidified water, the reaction product was dried and fractionally distilled to give 2 fractions:

Fr. I, b.p. 93 – 94° (3 mm); d_4^{20} 0.8118; n_D^{20} 1.4560
Fr. II, b.p. 174 – 176° (3 mm); d_4^{20} 0.8482; n_D^{20} 1.4769
Residue: an oily liquid

Fraction I gave the following Raman spectrum: 447 (2), 569 (5 br) 606 (4), 720 (4 br), 803 (4), 963 (3 br), 1013 (4 br), 1082 (2 br), 1116 (4), 1231 (4 br), 1306 (2), 1326 (3), 1374 (3), 1413 (4), 1435 (4), 1462 (6), 2175 (10).

Of these frequencies, that of 2175 (10) belongs to the triple bond in the α-position to the silicon; there are no double bonds in the spectrum. From Stepanov's work [9] we know that simple branching (tertiary carbon atom −CH−) is characterized by frequencies of 1140 cm^{-1} and 1170 cm^{-1}; on the other hand, Egorov and Bazhulin [8] report spectra of β-allylpropyltrimethylsilane and β-allylpropyltriethylsilane which actually contain the frequencies of 1129 (2) and 1185 (4) and which must evidently be attributed to simple branchings of the molecules in question. The spectrum of fraction I with b.p. 93 – 94° (3 mm) does not contain any of these frequencies and consequently we can assume that fraction I is triethyl-1-octynesilane, formed according to the scheme:

$$(C_2H_5)_3Si-C{\equiv}C-CH{=}CH_2 + LiC_4H_9 \longrightarrow (C_2H_5)_3Si-C{\equiv}C-\underset{Li}{CH}-CH_2\cdot C_4H_9 \xrightarrow{H_2O} (C_2H_5)_3Si-C{\equiv}C-CH_2-CH_2-C_4H_9.$$

In Table 5 are set forth the analytical data for triethyl-1-octynesilane.

Originally we suggested that the fraction with b.p. 174 – 176° (3 mm) was the result of addition of 2 moles of C_4H_9Li according to the scheme:

$$(C_2H_5)_3Si-C{\equiv}C-CH{=}CH_2 + 2C_4H_9Li \longrightarrow (C_2H_5)_3Si-\underset{Li}{\overset{C_4H_9}{C}}{=}\underset{Li}{CH}-CH_2\cdot C_4H_9 \xrightarrow{H_2O} (C_2H_5)_3Si-CH{=}\underset{C_4H_9}{C}-CH_2-CH_2\cdot C_4H_9,$$

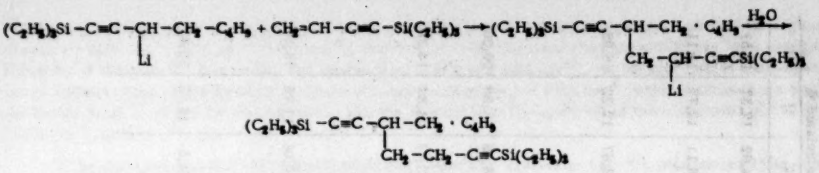
i.e. a product with the composition $C_{18}H_{32}Si$. The infrared spectrum of this fraction and its elementary analysis, however, did not confirm this suggestion.

In the spectrum was detected an intense absorption band at about 4.6μ which was unequivocal evidence of the presence of the C≡C linkage. The Raman spectrum in turn exhibited the stable C≡C frequency of 2175 cm^{-1} and did not contain the frequencies in the 1600 cm^{-1} region which are characteristic of the double bond. The elementary composition of this fraction corresponded to the formula $C_{24}H_{46}Si_2$, i.e. to a diacetylenic disilane apparently formed by interaction of the alkynyllithium with the original vinylethynylsilane according to the scheme:

TABLE 5

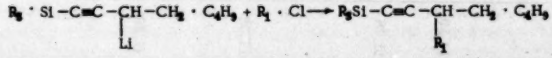
Properties of Acetylenic Mono- and Disilanes and of Diacetylenic Di- and Trisilanes

Substance	B.p. in °C (p in mm mercury)	d_4^{20}	n_D^{20}	MR found	MR calculated	Found % C	Found % H	Found % Si	Calculated % C	Calculated % H	Calculated % Si
Triethyl-1-octynesilane $(C_2H_5)_3Si-C\equiv C-CH_2\cdot CH_2\cdot C_4H_9$	93.5-94 (3)	0.8118	1.4560	75.14	74.97	74.98	12.62	12.37	74.92	12.57	12.51
Triethylisododecynesilane $(C_2H_5)_3Si-C\equiv C-CH(C_2H_5)-CH_2-C_4H_9$	98-99 (3)	0.8069	1.4520	84.40	84.23	76.01	12.62	11.27	76.11	12.77	11.11
Triethyl-(γ-trimethylsilyl-δ-butyl)-vinylethynylsilane $(C_2H_5)_3Si-C\equiv C-CH(Si(CH_3)_3)-CH_2C_4H_9$	108-109.5 (3)	0.8180	1.4555	98.44	98.49	69.56	12.39	16.96	68.87	12.22	18.92
Trimethyl-1-pentynesilane $(CH_3)_3Si-C\equiv C-CH_2-CH_2\cdot CH_3$	65-67 (52)	0.7597	1.4263	47.34	46.89	68.46	11.59	18.78	68.49	11.50	20.00
Triethyl-(γ-triethylsilylbutynyl-δ-butyl)-vinylethynylsilane $(C_2H_5)_3Si-C\equiv C-CH(CH_2\cdot C_4H_9)-CH_2-CH_2-C\equiv CSi(C_2H_5)_3$	174-176 (3)	0.8482	1.4769	129.90	129.29	73.77	11.78	14.43	73.77	11.87	14.36
The diacetylenic trisilane $(C_2H_5)_3Si-C\equiv C-CH(CH_2\cdot C_4H_9)-CH_2-CH(Si(CH_3)_3)-C\equiv C\cdot Si(C_2H_5)_3$	255-258 (3)	0.8739	1.4880	207.30	207.13	71.26	11.53	17.28	70.06	11.76	18.18
The diacetylenic disilane $(C_2H_5)_3Si-C\equiv C-CH(CH_2\cdot C_4H_9)-CH_2-CH(C_2H_5)-C\equiv C-Si(C_2H_5)_3$	181-182 (4)	0.8424	1.4720	139.10	138.6	74.17	11.96	13.69	74.5	12.03	13.47

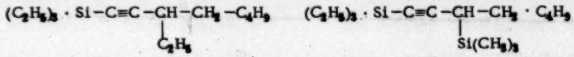


The analytical data of this fraction are set forth in Table 5.

We may note that the above-mentioned alkynyllithium readily condensed both with alkyl halides and with trialkyl-halogenosilanes according to the general scheme:



a secondary product being the above-noted diacetylenic disilane. In this manner we synthesized the monosilane (V) and the disilane (VI).

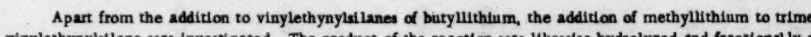


(V) (VI)

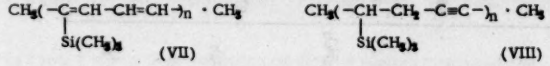
The properties and analytical data of these compounds are set forth in Table 5. Disilane (VI) is a representative of the unsymmetrical acetylenic disilanes similar in structure to the symmetrical disilanes which were recently synthesized by Petrov and Shchukovskaya [10] and simultaneously by Frisch and Joung [5] by condensation of trialkyl-halodisilanes with the symmetrical complex of Iotsich.

The above-mentioned lithium derivative was subjected not only to hydrolysis but also to alkylation with both C_2H_5Br and Cl·Si$(CH_3)_3$; the resultant disilane and trisilane are included in Table 5.

Apart from the addition to vinylethynylsilanes of butyllithium, the addition of methyllithium to trimethyl-vinylethynylsilane was investigated. The product of the reaction was likewise hydrolyzed and fractionally distilled. The yield of trimethyl-1-pentynesilane was small. The properties of this silicohydrocarbon



(the fourth conpound listed in Table 5) were similar to those of the silicohydrocarbon recently synthesized by another route by Frisch and Joung [5]. Distillation of this silicohydrocarbon did not yield any higher fractions such as were observed in the case of addition of butyllithium, while the main product of the reaction (the "residue") very quickly changed into an oxygen-containing, sticky polymer with a yellowish-brown color. This poylmer, soluble in organic solvents and fusible, must evidently be assigned the structure of (VII) or (VIII):



(VII) (VIII)

SUMMARY

1. It was shown that vinylethynylmagnesium halide condenses in high yield with both trialkyl-halogenosilanes and with aryldialkyl-halogenosilanes, monoalkyl-halogenosilanes, and even with silicon tetrachloride.

2. All the vinylethynylsilanes, and with particular ease divinylethynylsilanes, polymerize spontaneously on standing in the air to form transparent, peroxide-containing resins. Vinylethynylsilanes are capable, however, of polymerizing even in absence of air when heated in sealed tubes to 100°.

3. The velocities of polymerization of the vinylethynylsilanes were correlated with their structure. In the trialkylvinylethynylsilanes the rate of polymerization rises with increasing length of radical from methyl through butyl. In the dimethylarylsilane series it falls from phenyl to benzyl and from α-naphthyl to p-tolyl.

4. Selective hydrogenation of triethylvinylethynylsilane gave triethylbutadienylsilane and triethylbuten-2-silane.

5. In the bromination of vinylethynylsilanes the first two atoms of bromine add on at the triple bond, leading to polymerizable derivatives of the butadiene type. HCl at −70° also adds on but in the proportion of two molecules, forming a dichloride structurally analogous to that obtained by addition of 2 moles HCl to 1-buten-3-yne.

6. In contrast to hydrogen, bromine and hydrogen halides, which first add on at the triple bond, alkyllithiums only add on at the double bond of the enyne grouping. The resultant alkynyllithiums can be hydrolyzed by water or alkylated by alkyl halides to form silicohydrocarbons of the acetylenic series; their alkylation with trialkylhalogenosilanes gives unsymmetrical acetylenic disilanes. Diacetylenic disilanes are got from the alkynyllithium (via addition of butyllithium).

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Received May 6, 1953.

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* See Consultants Bureau Translation, p. 1603.

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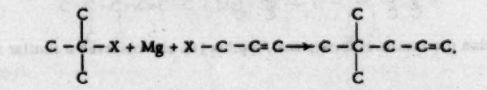
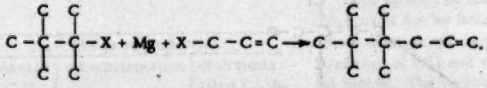
SYNTHESIS OF PARAFFINIC HYDROCARBONS WITH TWO ADJACENT QUATERNARY CARBONS

A. D. Petrov and L. I. Lavrishcheva

Organomagnesium synthesis of pure paraffinic hydrocarbons containing two adjacent quaternary carbons is a matter of considerable difficulty [1]. Whereas condensation according to reaction (1) proceeds with a yield of 85%, that according to reaction (2) proceeds with a yield of only 4%.

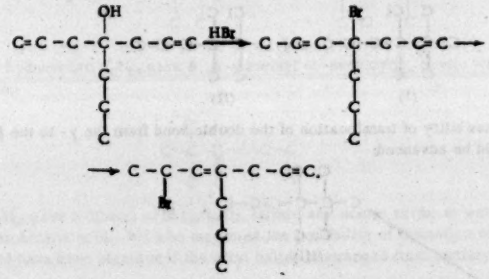


(1)



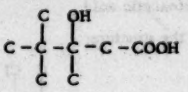
(2)

Since it is immaterial for the purpose of synthesis whether the double bond which activates the condensation is at the primary or tertiary halogen, it was decided to study the behavior in this reaction of unsaturated tertiary halides of various structures. It was found that whereas in the synthesis of the halohydrin from dimethylallylcarbinol there was scarcely any isomerization of the allyl radical into propenyl and the resultant halide containing a double bond in the γ-position proved incapable of entering into condensation, the preparation of the bromohydrin from diallylpropyl carbinol was accompanied by translocation of the double bond into the β-position in one of the allyl radicals. This rendered the halide active, but simultaneously, due to the allylic rearrangement, the halide structure was altered:

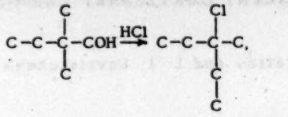


(3)

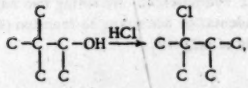
Instead of 4-bromo-4-propyl-1,5-heptadiene, there was formed 4-propyl-6-bromo-1,4-heptadiene, the condensation of which had previously failed to give a quaternary carbon [2]. This difference in behavior of tertiary alcohols of differing structures containing allyl radicals toward hydrogen halides led us to search for tertiary alcohols, containing allyl radicals, the formation from which of halohydrins would proceed with migration of the double bond to the β-position but without the accompaniment of the allylic rearrangement. Such an alcohol was found in methyl-tert-butylallylcarbinol which proved to be a convenient starting material for the synthesis of hydrocarbons containing two quaternary carbons. Methyl-tert-butylallylcarbinol was first prepared by Gnedin [3] who also established its structure by oxidizing it to the hydroxy acid:



In the preparation of the chlorohydrin from methyl-tert-butylallylcarbinol, we made use of the observations of Favorsky [4] and Whitmore [5] who showed that primary and secondary branched alcohols of the type of tert-R—COH and tert-R—$\underset{R_1}{\overset{|}{C}}$—OH undergo rearrangement on substitution of the hydroxyl group by halogen and are transformed into tertiary halides:

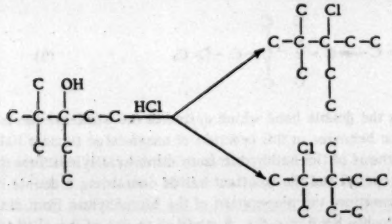


(4)



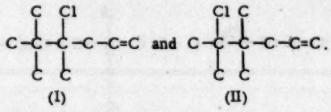
(5)

We also took into consideration the results of Brown and Fletcher [6] who observed a similar rearrangement of tertiary alcohols:



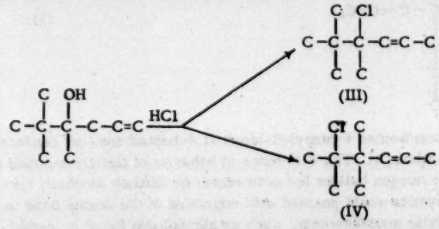
(6)

The behavior of branched olefinic alcohols had not previously been investigated; by analogy with the above-cited facts we thought that we might here also be able to obtain two chlorides:



(I) (II)

Moreover, allowing for the possibility of translocation of the double bond from the γ- to the β-position, the following general reaction scheme could be advanced:

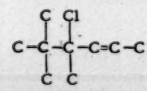


(III)

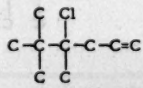
(IV)

Oxidation of the chloride with 1% aqueous $KMnO_4$ gave the following products: α, β, β-trimethyl-α-hydroxybutyric acid, β, β-dimethyl-α-oxobutyric acid, acetic acid, formic acid and much smaller amounts of pinacolone and oxalic acid. The products of oxidation exclude the presence of the chloride (IV) because we failed to detect α, α, β-trimethyl-β-hydroxybutyric acid and dimethylacetoacetic acid.

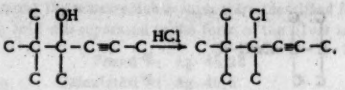
Consequently the chloride must be assigned the structure:



with a small admixture of

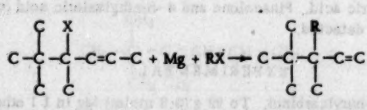


It should be mentioned that Zakharova [7] and Favorskaya [8] studied the interaction of acetylenic alcohols of similar structure with hydrochloric acid; investigation of the structure of the halohydrins showed that they do not suffer rearrangement and give only one chloride:



(7)

Reaction of the chloride prepared by us with RMgX enabled the synthesis of hydrocarbons containing two adjacent quaternary carbon atoms according to the scheme:



(8)

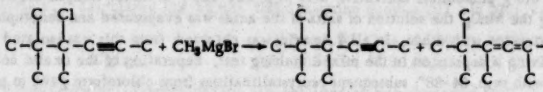
where R is allyl and propyl.

TABLE

Reaction of chlorides C	Yields of products		
	of cleavage HX $-C_9H_{16}$ in %	of condensation	of dimerization $C_{18}H_{34}$
(I) CH_3I	36	–	16%
(II) C_3H_5Br	20	30% $C_{12}H_{22}$	not detected
(III) C_3H_7Br	30	23% $C_{12}H_{24}$	5%

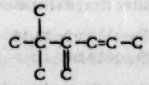
The product of reaction of the chloride with CH_3I could not be isolated in the pure form since the above reaction was accompanied by side reactions: cleavage of HCl and dimerization of the original allyl halide. The results of the reaction are set forth in the table.

Reaction (8) has the advantage over the similar reaction of Zakharova and Sapozhnikova [9] that it yields one hydrocarbon and not a mixture of acetylenic and allenic hydrocarbons:

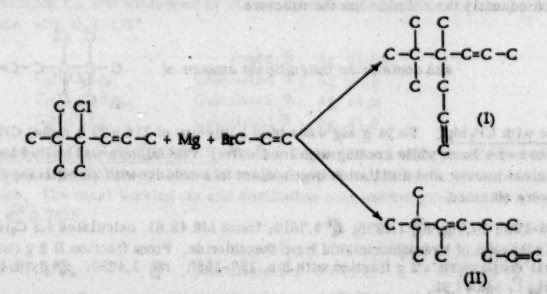


(9)

Oxidation of the hydrocarbon C_9H_{16} gave β, β-dimethyl-α-oxobutyric, acetic and formic acids; hence it can be assigned the structure:



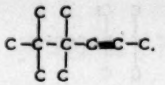
Oxidation of $C_{12}H_{22}$ gave a dibasic acid $C_9H_{16}O_4$, formic and acetic acids, as well as an insignificant amount of β, β-dimethyl-α-oxobutyric acid. We also suggested the possibility of formation of pinacolone and of methylsuccinic acid which should have been obtained if the allyl halide rearranged from tertiary to secondary:



(10)

The results of oxidation showed, however, that the reaction only proceeds according to the first scheme.

It should be noted that oxidation of the hydrocarbon $C_{12}H_{24}$ obtained by reaction with $C_9H_{17}MgBr$ proceeds with extraordinary difficulty. Here again we may draw a comparison with the acetylenic hydrocarbon obtained by Zakharova [9]:



Oxidation of $C_{12}H_{24}$ was effected with 2, 4 and 6% $KMnO_4$ and each time only 20-25% of the charge of hydrocarbon was oxidized, the remainder being recovered unchanged. The oxidation yielded a monobasic acid $C_{10}H_{20}O_2$ and traces of β, β-dimethyl-α-oxobutyric acid. Pinacolone and α-methylvaleric acid (products which should have been formed by rearrangement) were not detected.

EXPERIMENTAL

Synthesis of methylallyl-tert-butylcarbinol. To 92 g (3.8 moles) Mg in 1 l ether was added in the course of 14 hours a mixture of 260 g allyl chloride and 201 g pinacolone. The mixture was boiled for 8 hours and was decomposed with iced water and 10% HCl. Yield 219 g (77% of the theoretical) of alcohol with b.p. 168-172°; n_D^{20} 1.4452. Literature data [3]: b.p. 168.4°; n_D^{20} 1.4476; d_4^{20} 0.85508 and b.p. 169.5-170°; n_D^{20} 1.4452; d_4^{20} 0.8553.

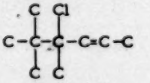
Hydrochlorination of 2, 2, 3-trimethyl-5-hexen-3-ol. 247 g alcohol was saturated with dry HCl in presence of Na_2SO_3 at 0-3°. Yield 216 g chloride in a yield of 80%. The chloride (here prepared for the first time) had the constants: b.p. 46-47° (6 mm); n_D^{20} 1.4575; d_4^{20} 0.9101.

	Found %: Cl 22.3; 21.7
$C_9H_{17}Cl$.	Calculated %: Cl 22.06

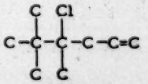
Oxidation of the chloride. 15 g chloride was emulsified in 400 ml water and addition was made of 5 g KOH and (portionwise) 44 g $KMnO_4$. The neutral products of oxidation were distilled off with steam into a solution of 2,4-dinitrophenylhydrazine. Yield about 0.3 g pinacolone derivative with m.p. 124-125°. A mixed sample did not give a depression of m.p. After separating the MnO_2, the solution of salts of the acids was evaporated and decomposed with 20% H_2SO_4; the organic acids were extracted with ether. In all 4.5 g acids was obtained; from this was isolated 0.2 g oxalic acid with m.p. 99-100°, not giving a depression in the mixed melting test. Separation of the oxalic acid was followed by precipitation of crystals with m.p. 84-88°; subsequent recrystallizations from chloroform gave m.p. 141-142°, corresponding to α, β, β-trimethyl-, α-hydroxybutyric acid which did not give a depression of melting point in admixture with an authentic specimen. The acid for the mixed melting test was obtained by oxidation of 2,2,3,6,7,7-hexamethyl-3,6-diol-4-octyne [10]. The mother liquor, after separation of the crystals, was treated with 2,4-dinitrophenylhydrazine to give 1 g hydrazone which after recrystallization from alcohol had m.p. 171-172°.

	Found %: N 18.09; 18.14
$C_{12}H_{14}N_4O_8$.	Calculated %: N 18.08

The nitrogen content and the melting point of this compound correspond to the 2,4-dinitrophenylhydrazone of β, β-dimethyl-α-oxobutyric acid. The acid for the mixed melting test was obtained by Glucksman's method [11] of oxidation of pinacolone, and the 2,4-dinitrodiphenylhydrazone was prepared for the first time with m.p. 171-172°. The mixed melting test with the 2,4-dinitrophenylhydrazone of the product of oxidation of the hydrocarbon did not show a depression of m.p. Consequently the chloride has the structure



and contains an insignificant amount of



Reaction of the chloride with CH_3MgI. To 24 g Mg was added a mixture of 118 g (0.8 mole) CH_3I and 64 g (0.4 mole) chloride in the course of 4 hours while cooling with iced water. The mixture was heated for 10 hours at 40°. After working up in the usual manner and distillation over sodium in a column with an efficiency of 15 theoretical plates, the following were obtained:

Fraction I with b.p. 126-129°, 17.7 g; n_D^{20} 1.4275; d_4^{20} 0.7510; found MR 42.61; calculated for $C_9H_{16}I_2$ MR 42.98. This is the product of cleavage of hydrochloric acid from the chloride. From fraction II 8 g (with b.p. 138-158°) was separated after several distillations a 2 g fraction with b.p. 157-158°; n_D^{20} 1.4330; d_4^{20} 0.7604; found MR 47.74; calculated for $C_{10}H_{20}I$, MR 47.91.

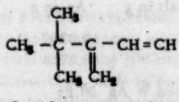
	Found %: C 85.80; H 14.20
$C_{12}H_{22}$.	Calculated %: C 85.62; H 14.38

Fraction III with b.p. 254-260° was obtained in a yield of 8.3 g; n_D^{20} 1.4615; d_4^{20} 0.8128. The structure of the hydrocarbons present in this fraction was not investigated.

Oxidation of C_9H_{16}. 10.8 g hydrocarbon was oxidized with 1% $KMnO_4$. A total of 52 g $KMnO_4$ was added instead of the calculated 65 g. Among the water-soluble acids were identified formic acid (by the calomel test) and acetic acid; the water-insoluble acid was separated in the form of the silver salt.

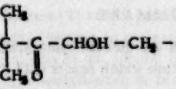
	Found %:	Ag 46.26
$C_9H_9O_2Ag$.	Calculated %:	Ag 45.5

The water-insoluble acid gave a 2,4-dinitrophenylhydrazone with m.p. 171-172°. These data identify the water-insoluble acid as β,β-dimethyl-α-oxobutyric acid and permit the diolefin to be assigned the following structure:



In addition to the acid a neutral product of oxidation was isolated: crystals with a camphor odor, m.p. 51°.

	Found %:	C 66.72; 66.70; H 11.57; 11.75
$C_9H_{16}O_2$.	Calculated %:	C 66.63; H 11.18

This is probably the ketoalcohol  , formed by oxidation of the tertiary bond.

Reaction of chloride with allyl bromide. A mixture of 106.5 g (2.3 moles) chloride and 136 g (1.12 moles) allyl bromide was added in the course of 11 hours to 48 g Mg. The mixture was then heated 10 hours at 40°. Working-up in the usual manner and fractionation in a column gave: 2-tert-butyl-1,3-pentadiene, 17 g, yield 20.6%; hydrocarbon of composition $C_{12}H_{22}$ 31.5 g, yield 28%; b.p. 176.5-178.5°; n_D^{20} 1.4420; d_4^{20} 0.7712; found MR 57.05; for $C_{12}H_{22}F_2$ calculated MR 56.68; found bromine number 201 and 200; calculated for $C_{12}H_{22}$ 193.

	Found %:	C 86.92; 86.80; H 13.20; 13.10
$C_{12}H_{22}$.	Calculated %:	C 86.66; H 13.34

2,2,3-Trimethyl-3-propylhexane was obtained by hydrogenation of $C_{12}H_{22}$ over nickel: b.p. 191-193° (756 mm); n_D^{20} 1.4310; d_4^{20} 0.7654; found MR 57.59; calculated for $C_{12}H_{26}$ MR 51.62.

	Found %:	C 84.86; 85.04; H 14.76; 14.94
$C_{12}H_{26}$.	Calculated %:	C 84.61; H 15.39

The solidifying temperature of 2,2,3-trimethyl-3-propylhexane was below −70°. In the case of the close (but less asymmetrical) structural analog 2,2,3,3,-tetramethylhexane the solidifying temperature is −54° [12].

Oxidation of $C_{12}H_{22}$. 10 g hydrocarbon was oxidized with 2% $KMnO_4$ solution. No neutral products of oxidation were isolated. Formic and acetic acids were identified among the acidic products, also a fraction of high-molecular acids with b.p. 140-150° (5 mm), consisting of structurally similar dibasic acids of the composition $C_9H_{16}O_4$ and $C_{10}H_{18}O_4$ with a trace of β,β-dimethyl-α-oxobutyric acid. The presence of the latter, due to contamination with hydrocarbon C_9, was evidenced by the too-low content of silver and also by formation of a 2,4-dinitrophenylhydrazone with m.p. 171°.

	Found %:	Ag 51.25
$C_9H_{14}O_4Ag_2$.	Calculated %:	Ag 53.5
$C_{10}H_{16}O_4Ag_2$.	Calculated %:	Ag 51.6
$C_9H_9O_2Ag$.	Calculated %:	Ag 45.5

Reaction of chloride with $C_9H_{17}MgCl$. To 24 g Mg in 250 ml ether is added, over a period of 6 hours, a mixture of 134 g (1.1 moles) propyl bromide and 80.3 g (0.5 mole) of the chloride $C_9H_{17}Cl$. The mixture is heated at 35° for 7 hours. The usual working-up and distillation over sodium gave: 1) 19 g C_9H_{18}; yield 30%; b.p. 126-128°; n_D^{20} 1.4262; d_4^{20} 0.7515.

	Found %:	C 86.87; 86.85; H 12.93; 12.85
C_9H_{18}.	Calculated %:	C 87.01; H 12.99

2) 20 g $C_{12}H_{24}$; yield 23%; b.p. 177-179°; n_D^{20} 1.4328; d_4^{20} 0.7594; found MR 57.57; calculated for $C_{12}H_{24}$ MR 57.15.

MR 57,15,

Found %: C 85,39; H 14,49; 14,51

$C_{12}H_{24}$. Calculated %: C 85,62; H 14,38

3) 3,2 g hydrocarbon with b.p. 250-260°; n_D^{20} 1,4610; d_4^{20} 0,8160; found MR 84,21; calculated for $C_{12}H_{24}$ MR 84,39.

Oxidation of $C_{12}H_{24}$. 10,5 g hydrocarbon was oxidized with 2% $KMnO_4$ solution. Oxidation proceeded very slowly and was continued for 8 days. Only acidic products were isolated; they were fractionated in the form of silver salts:

	Weight of salt in g	Ag, in g	Ag in %
Fraction I	0,0747	0,0297	39,76
Fraction II	0,0508	0,0254	50,0

$C_{10}H_{19}O_2$. Calculated % Ag 38,65

Fraction I corresponds to a monobasic acid with the composition C_{10}. Fraction II is apparently a mixture of acetic and β,β-dimethyl-α-oxobutyric acids, the latter originating from the presence of hydrocarbon C_9 formed by cleavage of HCl from the chloride.

SUMMARY

1. It was established that the tertiary halide of the alcohol synthesized from pinacolone and $MgBrC-C\equiv C$, is an active halide with a double bond in the β-position which reacts with RMgX in the tertiary form; the latter does not undergo the allyl rearrangement.

2. This characteristic of the halide in question, which differentiates it from the halide of dimethylallylcarbinol (in whose formation translocation of the double bond does not occur) and from other tertiary halides containing an allyl grouping which suffer the allylic rearrangement, enabled us to utilize the tertiary halide, 2-chloro-4, 5,5-trimethyl-2-hexene (prepared by us for the first time), in the synthesis of hydrocarbons containing two adjacent tertiary carbons.

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Received July 10, 1953

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* See Consultants Bureau Translation, p. 1843.
** " " " " p. 949.

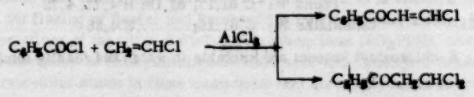
BRIEF COMMUNICATIONS

SYNTHESIS OF ARYL-β-CHLOROVINYL KETONES

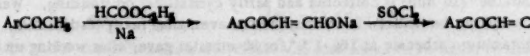
A. N. Nesmeyanov, N. K. Kochetkov and M. I. Rybinskaya

The diverse reaction possibilities of β-chlorovinyl ketones, manifested by the high mobility of the chlorine atom, the activity of the double bond and the simultaneous substitution of the oxygen of the carbonyl group, make β-chlorovinyl ketones suitable starting materials for the synthesis of compounds of the most diverse classes [1]. It is therefore entirely natural that attempts should be made to broaden the possibilities of new methods of organic synthesis on the basis of β-chlorovinyl ketones by utilizing new representatives of the class of β-chlorovinyl ketones. Up to now the transformations of β-chlorovinyl ketones have been studied mainly with reference to alkyl-β-chlorovinyl ketones, whose synthesis we recently described [1]. In the present paper we describe the synthesis of aryl-β-chlorovinyl ketones, the reactions of which do not differ from those of their aliphatic analogs.

In the patent literature there is reference [2] to the possibility of obtaining phenyl-β-chlorovinyl ketone by condensation of benzoyl chloride with vinyl chloride in presence of aluminum chloride by the Kondakov-Krapivin reaction. Numerous repetitions of this synthesis in our laboratory led to negative results, and this lack of success is confirmed in the work of other authors [3]. Condensation of benzoyl chloride with vinyl chloride, conducted in various conditions, leads to a difficulty resolvable mixture of phenyl-β-chlorovinyl ketone and phenyl-β,β-dichloroethyl ketone from which the chlorovinyl ketone can only be isolated in low yield:



Panizzi [3] used an old method of Claisen [4] for synthesis of phenyl-β-chlorovinyl ketone. Claisen obtained phenyl-β-chlorovinyl ketone by treating hydroxymethylene acetophenone with thionyl chloride [5] but he did not give a detailed account of his procedure. An exhaustive investigation of this reaction enabled us to establish the precise conditions for synthesis and to extend it to other hydroxymethylene ketones, so that we were able to develop a general method of synthesis of aryl-β-chlorovinyl ketones according to the scheme:



It was found more convenient to isolate the sodium enolate of the hydroxymethylene ketone, to free it from unreacted substituted acetophenone by repeated washing with ether, and only after this treatment to bring it into reaction with thionyl chloride. In this manner we succeeded in obtaining aryl-β-chlorovinyl ketones in satisfactory yields. By this method, starting from acetophenone, p-tolylmethyl ketone, p-bromoacetophenone and p-methoxyacetophenone, we obtained (respectively) phenyl-, p-tolyl-, p-bromophenyl- and p-methoxyphenyl-β-chlorovinyl ketones in yields of 30-60%.

These aryl-β-chlorovinyl ketones are high-boiling liquids or readily fusible solids (p-bromophenyl- and p-methoxyphenyl-β-chlorovinyl ketones), considerably more stable in storage than their aliphatic analogs. Their reactivity is apparently rather lower than that of the alkyl-β-chlorovinyl ketones, but the character of the chemical behavior itself is perfectly analogous, as we were able to show when using them for the synthesis of flavine salts; on the basis of p-methoxyphenyl-β-chlorovinyl ketone was obtained a natural anthocyanidin, while the methyl ether gave hesperidin [6].

EXPERIMENTAL

Phenyl-β-chlorovinyl ketone. To a suspension of 5.0 g finely pulverized sodium, 17.0 g ethyl formate and 100 ml absolute benzene were added dropwise, with energetic stirring and with cooling, 24.0 g acetophenone in

benzene (1:1). After 3 hours' stirring at room temperature, the precipitate of sodium salt of hydroxymethylene acetophenone was quickly filtered, washed with absolute ether, transferred again to the flask, covered with benzene and decomposed by cautious addition of water and then of 10% sulfuric acid. The benzene layer was dried over calcium chloride and filtered; then 26.0 g thionyl chloride was added and the mixture heated on a water bath until hydrogen chloride ceased to come off; this required about 5 hours. The benzene was distilled off and the residue distilled in vacuum to give 16.5 g (50% of the theoretical) of phenyl-β-chlorovinyl ketone with b.p. 118-120° (10 mm); n_D^{20} 1.5742. Literature data [4]: b.p. 125-127° (18 mm).

p-Tolyl-β-chlorovinyl ketone is similarly prepared from 50.0 g p-tolylmethyl ketone, 36.0 g ethyl formate, 10.0 g sodium in 200 ml benzene and 50.0 g thionyl chloride. Yield 24.0 g (30% of the theoretical) of substance with b.p. 118-120° (5 mm); n_D^{20} 1.5826; d_4^{20} 1.1680.

	Found %:	C 66.55;	66.29;	H 5.23; 5.06
$C_{10}H_9OCl$.	Calculated %:	C 66.46;		H 5.02

p-Bromophenyl-β-chlorovinyl ketone is similarly prepared from 40.0 g p-bromoacetophenone, 19.0 g ethyl formate, 4.6 g sodium in 150 ml benzene and 35 g thionyl chloride. The residue remaining after removal of the benzene crystallized. After recrystallization from ligroine, p-bromophenyl-β-chlorovinyl ketone forms fine needles with m.p. 38.5-39.5°; yield 19.0 g (40% of the theoretical).

	Found %:	C 43.88;	44.00;	H 2.55; 2.42
C_9H_6OClBr.	Calculated %:	C 44.02;		H2.46

p-Methoxyphenyl-β-chlorovinyl ketone is prepared similarly from 16.0 g p-methoxyacetophenone, 16.0 g ethyl formate, 2.5 g sodium in 100 ml benzene and 30.0 g thionyl chloride. After vacuum distillation [b.p. 154-157° (3 mm)] the substance crystallized; recrystallization from ligroine gave lustrous needles with m.p. 47-48°; yield 12.5 g (60% of the theoretical).

	Found %:	C 61.17;	61.18;	H 4.77; 4.72
$C_{11}H_9O_2Cl$.	Calculated %:	C 61.15;		H 4.55

All the prepared aryl-β-chlorovinyl ketones are insoluble in water and readily soluble in common organic solvents.

Reaction of benzoyl chloride with vinyl chloride. Into a solution of 19.0 g benzoyl chloride in 50 ml dry carbon tetrachloride with energetic stirring and cooling with iced water is passed a stream of dry vinyl chloride and addition is made in small portions in the course of an hour of 30.0 g aluminum chloride. After 4 hours' passage of vinyl chloride, a violent reaction suddenly sets in and the mixture boils. After six hours' saturation with vinyl chloride, the mixture is poured onto ice, the lower layer is separated, the aqueous layer is extracted with chloroform, the extracts are dried with calcium chloride, the solvent is distilled off and the residue is distilled in vacuum. A fraction with b.p. 130-150° (10 mm) is collected and partly crystallizes on standing. Weight 15.0 g. Pure phenyl-β-chlorovinyl ketone could not be isolated from this fraction even after many distillations. Heating of the product with 10.0 g calcined potassium carbonate at 150-170° for 30 minutes gave, after working up in the usal manner, 5.1 g not perfectly pure phenyl-β-chlorovinyl ketone with b.p. 123-127° (10 mm).

SUMMARY

A method was developed for the synthesis of aryl-β-chlorovinyl ketone by condensation of substituted acetophenones with ethyl formate followed by treatment of the resultant hydroxymethylene ketone with thionyl chloride.

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Received February 23, 1954.

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THE ATOMIC REFRACTION OF PHOSPHORUS AND SULFUR IN POLYTHIOPHOSPHOÖRGANIC COMPOUNDS

M. I. Kabachnik, T. A. Mastryukova and E. I. Godyna

In a previous communication [1] we derived the values of the atomic refraction of phosphorus and sulfur in some thiophosphoörganic compounds. As we know, in esters, chloranhydrides and other derivatives of oxy acids of phosphorus the atomic refraction of phosphorus retains a constant value within a specific group of compounds [2]. Thus it is constant in derivatives of phosphoric acid (3.76 for the sodium D line), phosphorous acid (7.04), alkylphosphonic acids (4.27). Constancy of the atomic refraction of phosphorus in these compounds is manifested only when the character of the bond of the other elements with phosphorus is taken into account in the calculation. For example, for the chlorine atom it is necessary to assume a value of the atomic refraction characteristic of chlorine in chloroanhydride combination (6.336 derived from the molecular refraction of the haloanhydrides of carboxylic acids [3]), since the bond between chlorine and phosphorus bears the character of a haloanhydride bond. In derivatives of phosphoric acid the atomic refraction of the oxygen linked by a double (semi-polar) bond with phosphorus is equal to 2.211, as in ketones, and the carbonyl group of carboxylic acids. The literature contains many data for the thiophosphoörganic compounds. In a paper by Jones, Davies and Dyke [4] the value for the refraction of sulfur in thiophosphates is given as 9.68 (sodium D line).

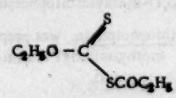
Our study of the dialkylthiophosphites $(RO)_2PSH$ [5] has shown that the molecular refraction of compounds of this class can be calculated with satisfactory accuracy if a value of 9.70 is assumed for the atomic refraction of sulfur in accordance with the finding of Boudet and Rambaud [6] for thioketonic sulfur. In addition a study of the refraction of many representatives of the class of dialkyldithiophosphates $(RO)_2PSSH$, trialkyldithiophosphates $(RO)_2PSSR$ and mixed thioanhydrides of dialkyldithiophosphoric acid and carboxylic acids $(RO)_2PSSCOR'$ [1] showed that the refraction of the two sulfur atoms in these compounds was invariably equal to the refraction of the two sulfur atoms in purely carbon compounds possessing a similar structure. Thus, for trialkyldithiophosphates the group refraction for S_2 was found to be the same as that of esters of xanthic acid [7,8]:

$AR_{S_2} = 18.72$

$AR_{S_2} = 18.67 - 18.78$

The refraction of the sulfur atoms in mixed anhydrides was also found to be equal to that in the corresponding purely carbon compound [8]:

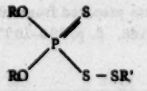
$AR_{S_2} = 19.77$



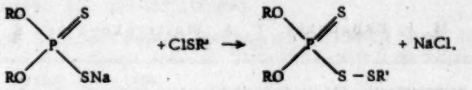
$AR_{S_2} = 19.53$

It appeared to be a matter of very great interest to establish whether the observed regularity is a general one. If this should be the case, then investigations in the field of phosphoörganic compounds would be considerably facilitated, and also there would be more opportunities for a comparative study of the problems of the reciprocal influence of atoms in phosphoörganic and in purely carbon compounds of the same type.

As a fresh object of investigation we chose the S-alkylthio-O,O-dialkylthiophosphates with the following structure:



The analogous purely carbon compounds are known. Thus, for methylthioacetyldisulfide $CH_3-C(=S)-S-SCH_3$ the group refraction of the three sulfur atoms, according to two authors is 27.68 [9] and 28.02 [6]. We realized the synthesis of the required S-alkylthio-O,O-dialkylthiophosphates by reaction of dialkyldithiophosphates of alkali metals with aliphatic sulfenyl chlorides [10]:



These are transparent liquids with a more or less deep-yellow color; they are soluble in carbon tetrachloride and benzene, insoluble in water; their constants are set forth in the table

TABLE 1

Formula	B.p. in °C (p in mm mercury)	Yield in %	n_D^{20}	d_4^{20}	MR	AR_S
$(C_2H_5O)_2PS_2CH_3$	100.5-101.5 (2.5)	41	1.5500	1.2142	60.93	27.49
$(i\text{-}C_3H_7O)_2PS_2CH_3$	99-100 (2)	60	1.5297	1.1471	70.09	27.42
$(C_2H_5O)_2PS_2C_2H_5$	106-107 (3)	39	1.5431	1.1810	65.76	27.68
$(i\text{-}C_3H_7O)_2PS_2C_2H_5$	117-118 (3.5)	48	1.5240	1.1189	75.05	27.75
$(C_2H_5O)_2PS_2C_4H_9$	139.5-140 (3.5)	30	1.5306	1.1246	75.33	28.03
$(i\text{-}C_4H_9O)PS_2C_2H_5$	129-130 (2.5)	22	1.5183	1.0866	84.39	27.85

The probable mean value of the group refraction for the three sulfur atoms was calculated from the data in the tables; it is equal to 27.70 ± 0.15.

Consequently even for such complex compounds as the investigated S-alkylthio-O,O-dialkyldithiophosphates, the value of the atomic refraction of the atoms linked to phosphorus is, within the limits of experimental error, equal to that in purely carbon compounds of the corresponding type.

EXPERIMENTAL

Preparation of S-alkylthio-O,O-dialkyldithiophosphates. The alkylsulfenyl chlorides were prepared by the patented method [10]. To the sodium or potassium dialkyldithiophosphate in a small quantity of carbon tetrachloride, with stirring and cooling to 10-5°, was added from a dropping funnel the equivalent amount of alkylsulfenyl chloride in carbon tetrachloride solution. Usually the alkylsulfenyl chloride at once entered into reaction, as marked by the disappearance of the bright-orange color. The reaction was later completed by heating the mixture on a water bath at 50-60° for 2 hours. After cooling, the precipitate was filtered and the filtrate fractionated in vacuum. Yield of S-alkylthio-O,O-dialkyldithiophosphates from 10 to 20%.

S-Methylthio-O,O-diethyldithiophosphate was prepared from 6.72 g (0.03 mole) potassium diethyldithiophosphate and 2.35 g (0.025 mole) methylsulfenyl chloride. B. p. 100.5-101.5° (2.5 mm); n_D^{20} 1.5500; d_4^{20} 1.2142; yield 2.45 g (41% of theoretical).

	Found %: P 13.41; 13.21	Found MR 60.93
$C_5H_{13}O_2PS_3$.	Calculated %: P 13.36	Calculated MR 61.14*

S-Methylthio-O,O-diisopropyldithiophosphate was prepared from 5.9 g (0.025 mole) sodium diisopropyldithiophosphate and 2.35 g (0.025 mole) methylsulfenyl chloride. B.p. 99-100° (2 mm); n_D^{20} 1.5297; d_4^{20} 1.1471; yield 3.5 g (60% of the theoretical).

	Found %: P 11.96; 11.93	Found MR 70.09
$C_7H_{17}O_2PS_3$.	Calculated %: P 11.92	Calculated MR 70.37

S-Ethylthio-O,O-diethyldithiophosphate was prepared from 26.9 g (0.12 mole) potassium diethyldithiophosphate and 12.5 g (0.12 mole) ethylsulfenyl chloride. B. p. 106-107° (3 mm); n_D^{20} 1.5431; d_4^{20} 1.1810; yield 11.2 g (39% of the theoretical).

*For calculation of the MR for the three sulfur atoms the value of 27.70 derived in this investigation was assumed.

	Found %:	P 12.78; 12.74	Found MR 65.76
$C_6H_{15}O_2PS_3$.	Calculated %:	P 12.60	Calculated MR 65.78

S-Ethylthio-O,O-diisopropyldithiophosphate was prepared from 11.8 g (0.05 mole) sodium diisopropyldithiophosphate and 7.7 g (0.08 mole) ethylsulfenyl chloride. B.p. 117-118° (3.5 mm); n_D^{20} 1.5240; d_4^{20} 1.1189; yield 6.6 g (48% of the theoretical).

	Found %:	P 11.25; 11.12	Found MR 75.05
$C_9H_{19}O_2PS_3$.	Calculated %:	P 11.31	Calculated MR 75.00

S-Butylthio-O,O-diethyldithiophosphate was prepared from 11 g (0.05 mole) potassium diethyldithiophosphate and 6.05 g (0.05 mole) butylsulfenyl chloride. B.p. 139.5-140° (3.5 mm); n_D^{20} 1.5306; d_4^{20} 1.1246; yield 3.9 g (30% of the theoretical).

	Found %:	P 11.17; 10.82	Found MR 75.33
$C_9H_{19}O_2PS_3$.	Calculated %:	P 11.31	Calculated MR 75.00

S-Ethylthio-O,O-diisobutyldithiophosphate was prepared from 26.4 g (0.1 mole) sodium diisobutyldithiophosphate and 12 g (0.12 mole) ethylsulfenyl chloride. B. p. 129-130° (2.5 mm); n_D^{20} 1.5183; d_4^{20} 1.0866; yield 6.6 g (22% of the theoretical).

	Found %:	P 10.38; 10.11	Found MR 84.39
$C_{10}H_{23}O_2PS_3$.	Calculated %:	P 10.36	Calculated MR 84.24

S-Methylthio-O,O-diisopropyldithiophosphate was prepared from 5.9 g (0.025 mole) of sodium diisopropyldithiophosphate and 2.35 g (0.025 mole) methylsulfenyl chloride. B.p. 99-100° (2 mm); n_D^{20} 1.5297; d_4^{20} 1.1471; yield 3.5 g (60% of theoretical).

	Found %:	P 11.96; 11.93	Found MR 70.09
	Calculated %:	P 11.92	Calculated MR 70.37

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Received March 13, 1954

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SYNTHESIS AND TRANSFORMATIONS OF ORGANOSILICON COMPOUNDS

COMMUNICATION 1. SYNTHESIS OF THE VINYL ETHER OF γ-HYDROXYPROPYLTRIMETHYLSILANE

M. F. Shostakovsky and I. A. Shikhiev

The synthesis and properties of vinyl ethers of organosilicon alcohols and silanols present great interest for synthetic organic chemistry. We are interested in the first place in vinyl ethers of silicoalcohols with the following general structure: $R_3Si(CH_2)_n-OH$, where R may be alkyl, aryl, or alkaryl, and n = 1,2,3, etc.

The synthesis of vinyl ethers of silicoalcohols can evidently be carried out in principle by the following routes:

$$HC\equiv CH + R_3Si(CH_2)_n-OH \rightarrow R_3Si(CH_2)_n-O-CH=CH_2.$$

$$CH_2=CHCl + NaO(CH_2)_nSiR_3 \rightarrow R_3Si(CH_2)_n-O-CH=CH_2.$$

Up to now the vinylation of silicoalcohols has not been described in the literature. The purpose of the present research is to study the possibility of vinylation of silicoalcohols by the method of Favorsky and Shostakovsky [1].

With the objective of studying the properties and transformations of vinyl ethers containing silicon, we resolved to prepare the vinyl ethers of silicoalcohols the character of the hydroxyl group of which is similar to that of the corresponding purely organic alcohols. On this basis we set ourselves the task of studying the vinylation of the alcohol with the following structure: $(CH_3)_3SiCH_2-CH_2-CH_2OH$.

We effected the vinylation of this alcohol by the method of Favorsky and Shostakovsky. The reaction proceeds according to the following equation:

$$HC\equiv CH + (CH_3)_3SiCH_2-CH_2-CH_2OH \rightarrow (CH_3)_3SiCH_2-CH_2-CH_2-O-CH=CH_2.$$

The resultant γ-hydroxypropyltrimethylsilyl vinyl ether was characterized by its physicochemical constants. In addition its structure was confirmed by hydrolysis, which proceeds as follows:

$$(CH_3)_3SiCH_2-CH_2-CH_2-O-CH=CH_2 \xrightarrow{HOH} CH_2-\overset{O}{\overset{\|}{C}}-H + (CH_3)_3SiCH_2-CH_2-CH_2OH.$$

EXPERIMENTAL*

1. Synthesis of γ-hydroxypropyltrimethylsilane $(CH_3)_3SiCH_2-CH_2-CH_2OH$

Into a flask containing Grignard reagent (prepared from 24 g (1 mole) magnesium in 800 ml absolute ether and 122 g (1 mole) α-chloromethyltrimethylsilane [2], cooled to −6°, was slowly passed (with constant stirring) over a period of 2 1/2 hours 84 g (2 moles) dry gaseous ethylene oxide. Since the reaction proceeded with violence, the temperature of the mixture was kept at about +8°. The reaction mass was left overnight. The next day the solid complex was decomposed, first with crude ether and then with 10% hydrochloric acid.

The ethereal layer was separated from the aqueous layer; the latter was extracted with ether and added to the upper ether layer.

The ethereal solution was washed with 1% aqueous sodium carbonate solution and then with water and dried over calcined potassium carbonate. After driving off the ether, the residue (128 g) was vacuum-distilled at 11-12 mm to give:

*Senior Technician Z. S. Volkova participated in the experimental work.

Fraction I	B.p. to 54°;	7.4 g;	n_D^{20} 1.4260
Fraction II	B.p. 55-63°;	21.8 g;	n_D^{20} 1.4296
Fraction III	B.p. 64-65°;	90.5 g;	n_D^{20} 1.4298
	Residue	3 g	

Fractions II and III were combined and redistilled to give 102 g (yield 77.3% of the theoretical) of a fraction with b.p. 62-63° (10 mm). It had the constants*: n_D^{20} 1.4298; d_4^{20} 0.8408; and consisted of γ-hydroxypropyltrimethylsilane.

2. Synthesis of γ-hydroxypropyltrimethylsilyl vinyl ether $(CH_3)_3SiCH_2-CH_2-CH_2-O-CH=CH_2$

20 g γ-hydroxypropyltrimethylsilane [b.p. 62-63° (10 mm), d_4^{20} 0.8408; n_D^{20} 1.4298], 2 g pulverized KOH and 60 g absolute dioxane were charged into a steel rotating autoclave of 0.5 liter capacity. The air was purged from the autoclave by a stream of acetylene and the autoclave was filled with acetylene from a cylinder under a pressure of 18-20 atm. until the reaction mixture was completely saturated with it at the indicated pressure at room temperature and with constant stirring. The reaction mixture was then heated to 180° and the reaction continued for 8 hours. The next day the autoclave was discharged, the product being obtained in the form of a darkish liquid which was washed 5 times with water and dried over sodium sulfate. Three distillations in vacuum gave a fraction with b.p. 60° (18 mm); n_D^{20} 1.4286; d_4^{20} 0.8168.

	Found:	MR 49.92
$C_8H_{18}SiO$:	Calculated	MR 50.10
	Found %:	C 60.66; 60.77; H 11.38; 11.10; Si 18.39; 18.60
$C_8H_{18}SiO$.	Calculated %:	C 60.69; H 11.46 Si 17.72

The above data agree with the formula for γ-hydroxypropyltrimethylsilyl vinyl ether, the mean yield of which from a series of experiments was 35%. γ-Hydroxypropyltrimethylsilyl vinyl ether is a transparent mobile liquid with a characteristic ethereal odor. It decolorizes a weak solution of $KMnO_4$ and bromine water. The conditions for its polymerization are being studied.

3. Hydrolysis of γ-hydroxypropyltrimethylsilyl vinyl ether

A weighed amount of the vinyl ether is put into a flask to which is added 25 ml 2% sulfuric acid and 25 ml 0.2 N sodium bisulfite; the flask is shaken until there is complete solution at 24°. At the end of 45 minutes the excess of sodium bisulfite is titrated with 0.1 N iodine.

Found acetaldehyde 90.58; 92.95% of the theoretical.

SUMMARY

1. Using γ-hydroxypropyltrimethylsilane as model substance, the possibility was established of vinylation of silicoalcohols by the method of Favorsky and Shostakovsky. γ-Hydroxypropyltrimethylsilyl vinyl ether was thus obtained.

2. The structure of γ-hydroxypropyltrimethylsilyl vinyl ether was confirmed by its hydrolytic cleavage.

3. Details are given of a method for preparation of γ-hydroxypropyltrimethylsilane and its stability to caustic alkalies is demonstrated.

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Received July 15, 1954.

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CHRONICLE

ANNUAL CONFERENCE OF THE INSTITUTE OF PHYSICAL CHEMISTRY OF THE ACADEMY OF SCIENCES OF THE UNION OF SSR

On March 25 in the Institute of Physical Chemistry of the Academy of Sciences USSR was held the annual conference of the institute at which Institute Director, Corresponding Member of the Acad. Sci., USSR, V.I. Spitsyn submitted a report on the over-all researches of 1953 and on some perspectives of research in 1954.

V. I. Spitsyn pointed out that in 1953 the greatest developments took place on problems traditionally associated with the institute and whose scope had expanded in the course of a number of years. These relate to investigations of surface phenomena and surface forces, the study of heterogeneous catalysis, the analysis of problems associated with the mechanism and kinetics of electrochemical processes, the study of corrosion processes and methods for combating them, as well as the new directions of research, developed in recent years, associated with problems of chromatography and radiochemistry. The report revealed the achievments of the institute both in respect of individual problems and of the plan as a whole. The reporter wished all concerned success in the achievement of new and theoretically valuable and economically useful results.

Corresponding Member of the Acad. Sci. USSR B.V. Deryagin in his address on the theme of : " The role of surface forces in the kinetics of heterogeneous systems " demonstrated from a unified and general standpoint the value of investigations of surface molecular and electrical forces for the examination and understanding of the mechanism and kinetics of processes in heterogeneous systems with variation of the magnitude or state of the surfaces of separation of the phases and without appreciable change of the masses and composition of the individual substances in the system. The opposite case of processes leading to changes of mass or composition of the components of the system (these include processes of corrosion, evaporation, condensation, topochemical processes, many electrochemical processes, catalytic processes, etc.) were classed by the reporter as first order processes in which the surface forces do not always play a decisive part, while in the case of equilibria they never do so.

With the help of a number of examples of practical value, he analyzed the decisive role of surface forces in the kinetics of first-order processes belonging to the category of surface phenomena proper. B. V. Deryagin drew attention to the specific role of surface forces in coagulation and adhesion of colloidal and dispersed substances, especially in liquid media. Precise information about this role became available after he and his coworkers, in 1934-37, detected and investigated the effect which they called the " wedging" pressure of thin films and which created an energy barrier hindering the approach of molecules to distances at which the resultant of the intermolecular attractions predominates.

The theory developed could be generalized for the case of coagulation of mixtures of colloids and the cohesion of diverse particles after establishment of the characteristics of these problems which are valuable for the theory of dyeing of fibers, the sizing of paper and other practical problems. Applying the same considerations, it was possible to bring precision to the theory of adhesion of bubbles to mineral particles which constitutes the basis of flotation of useful minerals.

Greater precision of the theory of coagulation requires clarification of the course of weakening of molecularforces between n interacting surfaces. This problem was treated by carrying out direct measurements of the attractive forces between n quartz and glass plates separated by an air space of the order of 10^{-4} cm and higher. These measurements led to important theoretical conclusions, in particular concerning the small influence of molecular forces on the velocity of coagulation of aerosols.

B. V. Deryagin showed that the adhesion of glue and protective films should be treated as a kinetic phenomenon; the thermodynamic approach leads to deviations from experimental results of 100-1000 times and more. The reporter pointed out the great current significance of the study of surface forces both for theory and for a number of very important national economic problems.

Doctor of Chemical Sciences A. V. Kiselev reported on " Adsorption on crystals and colloids" and showed that the current state of the science of adsorption is characterized by : 1) A gap between theoretical investigations of the external surfaces of crystals and the study of adsorption on the internal surfaces of porous bodies. Such a position not only

hinders the investigation of adsorption on the porous adsorbents and catalysts of the greatest practical importance but also limits the possibilities of theoretical study of adsorption. 2) Ignorance of the characteristics of the chemical nature and chemical variability of the surfaces of adsorbents.

The experimentally determined values of the adsorption and heat of adsorption of any given substance depend on the size of surface, the pore structure and the surface state of the adsorbent. The most important problem of adsorption is the separate measurement of : a) the transition from the experimentally measured relative magnitudes (per unit weight of surface) to the absolute magnitudes (per unit surface); b) the influence of shrinkage of pores on the absolute magnitudes of adsorption by investigation of these magnitudes for a series of adsorbents of identical character - ranging from nonporous to finely porous; c) chemical changes of the surface with unchanged pore structure.

In this connection A. V. Kiselev and co-workers made a systematic study of the absolute isotherms and heats of adsorption on quartz and silica gels with pore sizes of 200 to 20 A, on aluminosilica gels and on graphitic substances (soots, active carbons).

The reporter spoke of a number of researches which had established that the transition from quartz to large-pore silica gels does not appreciably change the absolute isotherms and heat of adsorption up to the start of capillary condensation . With further contraction of the pores of silica gels, the adsorptive potential is intensified. This intensification becomes extremely marked with reduction of pore size to 50 A, at first for larger molecules (hydrocarbons), and with further contraction of the pores also for small-sized molecules (nitrogen, methyl alcohol). In the case of adsorption of molecules of very small size which are mainly adsorbed at the expense of hydrogen bonds developed over short distances (water molecules), this effect is inappreciable. For adsorption from solutions, pore contraction in a number of cases causes strengthening of selective adsorption, for example in the separation of hydrocarbons. This is manifested by a shift of the maximum of the isotherms and by an increase in the energy of adsorption. Change in the degree of hydration of the surface of silica gels changes their adsorptive properties, particularly in respect of substances capable of forming hydrogen bonds with the hydroxyls of silica gel. On the surface of carbons, a sharp change of the absolute isotherms of adsorption of water vapor and methyl alcohol is caused by change of the degree of oxidation of the surface. In the case of active carbons the influence of the pore structure is superposed on this influence of the chemical nature of the surface.

THE DIAGRAM OF STATE OF THE TERNARY SYSTEM $BaO - Al_2O_3 - SiO_2$

N. A. Toropov, F. Ya. Galakhov and I. A. Bondar

The choice of the three-component system $BaO-Al_2O_3-SiO_2$ as the subject of this investigation was governed by a series of causes. First, the most important of the silicate systems are aluminosilicate compounds due to the great abundance of aluminosilicates throughout the earth's crust and the great variety of industrial silicate products. The relevance of this reason for our choice of the material of our investigation found confirmation in the course of the experimental work, in the earlier stages of which was established the congruence of the melting of mullite. Appropriate corrections were thereupon introduced into the fundamental physico-chemical silicate diagram of $Al_2O_3-SiO_2$.

The second reason was the high refractoriness of the majority of the compounds of the ternary system. This circumstance made the work difficult but at the same time endowed its results with great value. In fact, having developed a laboratory microfurnace of new design, we succeeded not only in investigating the system in question but also in devising a new method for the study of similar refractory systems. It was extremely interesting to compare the diagram with those of previously investigated aluminosilicate systems, as well as with the phase diagram of the system $BaO-B_2O_3-SiO_2$; the detection of complex three-component solid solutions in the system is likewise a matter of great scientific interest.

Of the three binary systems constituting the sides of the ternary diagram, we made a detailed study of the systems $Al_2O_3-SiO_2$ and $BaO-SiO_2$. In the system $Al_2O_3-SiO_2$ is formed the compound frequently encountered in industrial materials – mullite $3Al_2O_3 \cdot 2SiO_2$. This material was first discovered in the composition of porcelain – by Vernadsky [1] and later by Zemyatchensky [2]. The system as a whole was studied in most detail in 1924 by Bowen and Greig [3]. According to the data of these authors, mullite melts with decomposition; it forms a eutectic with silica.

Bauer, Gordon and Moor [4] obtained single crystals of mullite in the form of a boule 2 cm long and 1 cm thick. Fusion of a mixture corresponding to the composition of mullite was carried out in an oxy-hydrogen flame. The authors explain the formation of single crystals of mullite without separation of corundum by the rapid cooling from the temperature of melting to the temperature of crystallization of mullite. This explanation must, however, be rejected, since the crystallizing tendency of corundum is very high and it should certainly crystallize from melts of the mullite composition if the diagram of Bowen and Greig were correct.

The system $BaO-SiO_2$ has been closely investigated by Eskola [5]. The equilibrium relations between the phases were established by the quenching method. The author found a series of compounds in the system: $2BaO \cdot SiO_2$, $BaO \cdot SiO_2$, $2BaO \cdot 3SiO_2$ and $BaO \cdot 2SiO_2$. An equilibrium diagram was constructed on the basis of the investigation. The author indicates the formation of a solid solution between barium disilicate and dibarium trisilicate.

The phase diagram of the system $BaO-Al_2O_3$ has not been studied. Compounds of this system, however, are well known. Barium aluminates have been most completely studied by Toropov [6] who first established the existence of an aluminate of the composition $BaO \cdot 6Al_2O_3$.

The paper by Zimmer and Watts [7] has a direct bearing on the ternary diagram of $BaO-Al_2O_3-SiO_2$. These workers determined the melting point of the system by the cone deformation method. The portion of the diagram adjacent to the $BaO-SiO_2$ side was studied by Thomas [8] by the quenching method in combination with microscopic examination of the crystalline phases. Formation of a ternary solid solution between the barium silicates and celsian was observed, but the results of optical examination did not fully accord with the plotted vertical fields. The natural barium feldspar – celsian – with the composition $BaO \cdot Al_2O_3 \cdot 2SiO_2$ is the sole ternary compound in the system. Various authors have reported triclinic, monoclinic and hexagonal forms of celsian. The synthetic celsian obtained by Ginzberg [9] was a hexagonal variety with the refractive indices $Ng = 1.596$; $Np = 1.584$; $Ng - Np = 0.012$.

EXPERIMENTAL

Experimental Furnace. Preliminary tests on specimens from different parts of the diagram of the $BaO-Al_2O_3-SiO_2$ system showed that the greater proportion of the compositions possesses an initial crystallization temperature above 1500°. This circumstance called for an appropriate high-temperature furnace. For a number of reasons laboratory furnaces for temperatures higher than 1500° – Kryptol, graphite tubes, high-frequency – were unsuit-

able for investigations using the quenching method. A new furnace was therefore designed by one of the authors. This was a vacuum micro-furnace with a tungsten resistance giving a temperature of up to 2000°.

The pyrometer for determination of the temperature was graduated against specimens of known melting point in the form of pure metals – platinum, palladium, etc. and also certain compounds.

Furnace of temperatures up to 1600°. The heating element in this furnace was a 0,5 mm diameter wire composed of an alloy of platinum with 20% rhodium. The wire was wound round a sintered corundum, finger-shaped crucible with internal diameter 15 mm and length 100 mm. The crucible was mounted in a metal jacket packed with heat-insulating material. The sample of material to be tested, parcelled in platinum foil, was suspended directly from a platinum-platinorhodium thermocouple. The furnace was constructed at the close of the present investigation and was therefore not used in all cases.

Platinum resistance furnace. This normal annealing furnace, fitted with a device for dropping the sample into mercury, was used for up to 1450°. The temperatures in the two latter furnaces were measured with platinum-platinorhodium thermocouples and with galvanometers. The recordings of the thermocouples were checked by the method of heating of palladium, gold or silver wires.

Synthesis of specimens

The following starting materials were used: 1) silica in the form of a fine powder prepared from rock crystal. After heating, rapid cooling in water and pulverization in a steel mortar, the rock crystal was treated with dilute hydrochloric acid, washed with water and dried. Final pulverization was effected in an agate mortar. The product contained 99,90% SiO_2; 2) calcined alumina with a total content of impurities of 0,2%; 3) barium carbonate, chem. pure, containing 99,95% $BaCO_3$.

Preparation of homogeneous samples by fusion of mixtures of the components in platinum crucibles was ruled out due to their high melting points. Homogenization of the samples was therefore effected by fusion in an electric arc. Precisely weighed amounts of the starting materials (weighed on an analytical balance) were thoroughly mixed by co-grinding in a mortar; they were moistened with dextrin solution and shaped into 4-5 mm diameter rods with the help of a glass tube. After drying, the specimens were fused in an electric arc.

Method of investigation

The best method of studying the phase equilibria is the quenching method. It is difficult to employ, however, when crystallization of the melt takes place very quickly and the vitreous state cannot be stabilized. For the portions with high liquidus temperatures and a high rate of crystallization, the diagrams were therefore plotted from the melting points.

The melting point, determined by any desired method, is not always the true liquidus temperature. Only in the case of chemical compounds and of eutectic points does the melting point coincide with the liquidus temperature. Nevertheless if the melting points of a series of points are determined, then the general course of the liquidus curve can be revealed. The occurrence of an inflexion on such a curve indicates the existence of a eutectic or chemical compound at the turning point. Melting points were determined by a method specially developed for use with the micro-furnace.

Finally, for establishment of the primary phase in samples with a high liquidus temperature and a high speed of crystallization the following method was employed. The sample in the form of a small chip was placed in the micro-furnace as for determination of the melting point. Heating was applied until the sample melted, and the temperature was held for 0,5-2 min. The current was switched off and air was passed through the furnace to accelerate cooling; the container was quickly removed and the sample blown with air. If two crystalline phases were formed, as could be established by observation under the microscope, the experiment was repeated at higher temperatures until only one crystalline phase was obtained.

Examinations under the microscope were made for the most part on immersed preparations and rarely on polished sections. In some cases the data were supplemented by X-ray diagrams. The indices of refraction of the glasses were measured by the immersion method. Densities of the glassy products were determined with a pyknometer. In this case the glasses were taken in the form of chips and not in the pulverized state. The chemical stability of the glasses obtained in the system was determined in the following manner. Two glassy pellets (obtained in the arc) were measured along three mutually perpendicular directions and their surface was calculated. The pellets were charged into an exact volume (50 ml) of 0,005 N hydrochloric acid, and the solution was heated 30 minutes on a water bath and left at room temperature for 24 hours. The excess of acid was then titrated with alkali solution. The amount of acid combined per 100 mm^2 of specimen surface gave an approximate indication of its relative chemical stability.

Experimental Results

The study of the diagram was started from the fields bordering upon the binary systems. In the field round the binary system $BaO-SiO_2$ the boundary between the zones of stability of barium silicates followed a course in conformity with this system. The question of the position of the boundary between the fields of dibarium silicate and barium oxide remained unsettled.

In the region of the diagram from 75 to 93% barium oxide the melting points of a series of compositions were determined. The melting point of dibarium silicate was found to be 1730°. It gives a eutectic with barium oxide. The composition of the eutectic is : BaO 87% and SiO_2 13%; m.p. 1600°. The position of the fields on the $BaO-Al_2O_3$ side is likewise not inconsistent with the data for this system. Up to recently, however, the phase diagram itself of the system $BaO-Al_2O_3$ had not been established and it was studied in connection with the present investigation [10].

Finally, in the course of investigation of the field bordering on the $Al_2O_3-SiO_2$ side, the arrangement of the boundary curve between the mullite and corundum fields was observed to deviate from the position according to the generally accepted phase diagram of the system $Al_2O_3-SiO_2$. The occurrence of primary crystallization of mullite was observed in the field directly bordering upon the figurative point of its composition, whereas according to the old diagram [3] mullite melts with decomposition. This observation prompted a special investigation of the binary system in the portion with a high content of alumina [11].

Structure of the diagram of $BaO-Al_2O_3-SiO_2$

In the study of the ternary diagram 305 compositions were synthesized and subjected to test. The general form of the ternary diagram in percentages by weight with the plotted isotherms is shown in Figure 1. The whole diagram comprises 13 fields of stability of the following phases:

1. Tridymite (SiO_2)
2. Mullite ($3Al_2O_3 \cdot 2SiO_2$)
3. Corundum (Al_2O_3)
4. Barium hexaaluminate ($BaO \cdot 6Al_2O_3$)
5. Barium monoaluminate ($BaO \cdot Al_2O_3$)
6. Tribarium aluminate ($3BaO \cdot Al_2O_3$)
7. Barium oxide (BaO)
8. Dibarium silicate ($2BaO \cdot SiO_2$)
9. Monobarium silicate ($BaO \cdot SiO_2$)
10. Ternary solid solution ($2BaO \cdot 3SiO_2 - BaO \cdot 2SiO_2 - BaO \cdot Al_2O_3 \cdot 2SiO_2$)
11. Barium disilicate ($BaO \cdot 2SiO_2$)
12. Celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$)
13. Solid solution of an incongruent composition of composition ($3BaO \cdot 3Al_2O_3 \cdot 2SiO_2$)

In the field of the triangle was established the zone of primary crystallization of a hitherto unknown phase of variable composition ($3BaO \cdot 3Al_2O_3 \cdot 2SiO_2$). As we see from the diagram, the system contains two series of solid solutions, one of which is ternary and therefore a rarity among silicate systems. On the diagram are three (actual) binary systems: celsian-corundum; celsian-dibarium silicate; celsian-monobarium silicate. The fields of primary crystallization form 24 boundary curves. There are 11 binary eutectic points and 13 invariant points of which 4 are eutectic and 9 reaction points. The composition and temperature of the invariant points are given in Table 1. A part of the field of the triangle is occupied by compositions formed with sufficiently rapid cooling of the glass.

In Fig. 2 are plotted the curves corresponding to glasses with a constant refractive index; Fig. 3 relates to glasses of constant density; and Fig. 4 to glasses with constant chemical stability toward highly diluted hydrochloric acid. The boundaries between the fields of the region bordering upon the barium oxide corner were determined on the basis of the melting points and the course of the isotherms, and therefore the boundaries are indicated by broken lines. Determination of the primary phases by microscopic observation was unreliable due to the great velocity of crystallization and also to their chemical instability. The field of celsian and its figurative point occupy a central position in the triangle. Celsian crystallizes in the hexagonal modification described by Ginzberg [9]. Particularly good hexagonal plates were separated close to the boundaries of the field.

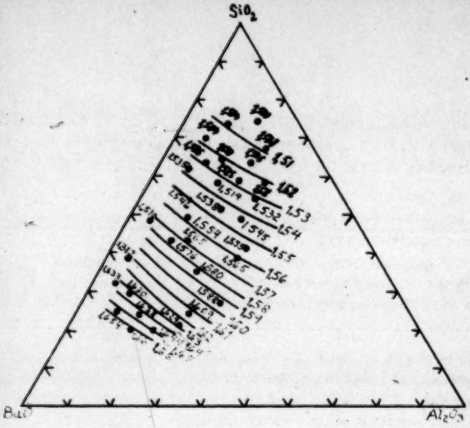

Fig. 2. Light refraction of glasses of the system $BaO-Al_2O_3-SiO_2$.

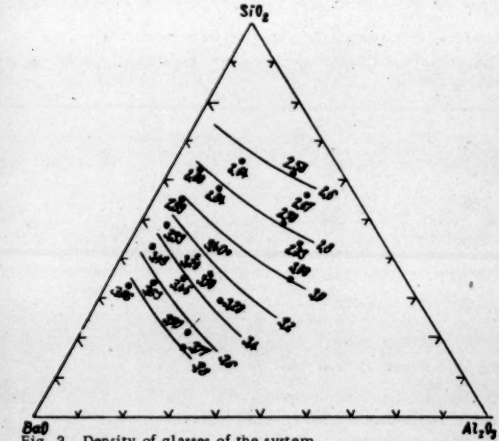

Fig. 3. Density of glasses of the system $BaO-Al_2O_3-SiO_2$

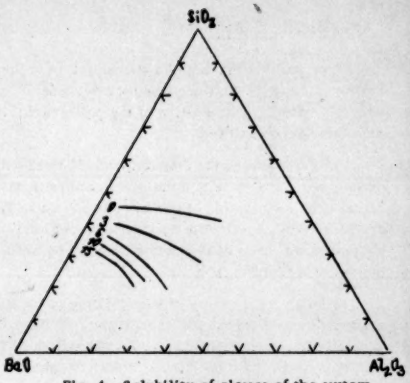

Fig. 4. Solubility of glasses of the system $BaO-Al_2O_3-SiO_2$ in dilute HCl (for the significance of the values see text).

A new ternary compound $3BaO \cdot 3Al_2O_3 \cdot 2SiO_2$.

Already during the preliminary study of the field of the triangle on the portion between the fields of celsian and barium monoaluminate there was observed crystallization of a previously unknown phase with variable optical constants, differing from all known compounds of the components of the system; this pointed to the presence of a solid solution. The clarification of the question as to which compounds form this solution proved to be extremely difficult. Attempts to isolate the new phase without admixture with other crystalline phases during complete crystallization did not lead to the desired result: it was always accompanied by other crystals.

Detailed study of many compositions from this region by the quenching method enables sufficiently accurate determination of its boundaries and of the character of the liquidus surface. The field of primary crystallization of the given phase takes the form of an elongated band whose maximum width occurs with a 3% change of concentration. A temperature peak at the liquidus surface could not be established; the temperature dropped uniformly from the corner of the field with the maximum content of alumina in the direction of the region of celsian and dibarium silicate. All these data, as well as the general position of the field among the other fields of the diagram indicate that not one of the known compounds of the system enters into the solid solution in question. There remained one possibility: the components of this solid solution (or at least one of them) are incongruent compounds. This hypothesis was supported by the direction of rise of the liquidus surface. The simplest formula in the assumed direction was $3BaO \cdot 3Al_2O_3 \cdot 2SiO_2$. A specimen of this composition when kept at 1050° for an hour crystallized in the form of one phase similar in crystalline structure to the solid solution concerned; it possessed the lowest optical constants: Ng = 1.624; Np = 1.615; Ng – Np = 0.009. Quenching of this specimen from 1600° only gave a grain of barium monoaluminate and a glass, which is fully understandable since the investigated composition lies in the region of primary crystallization of the monoaluminate. The temperature below which only the new phase crystallized and above which a glass remained was found to be 1500°.

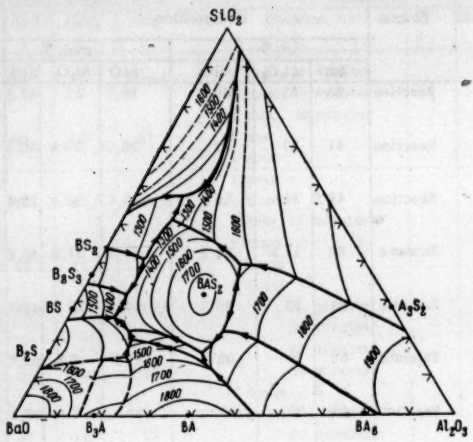

Fig. 1. Phase diagram of the system $BaO - Al_2O_3 - SiO_2$.

Fig. 6. Photomicrograph of section of the compound $3BaO - 3Al_2O_3 - 2SiO_2$ (crossed Nicols X 320).

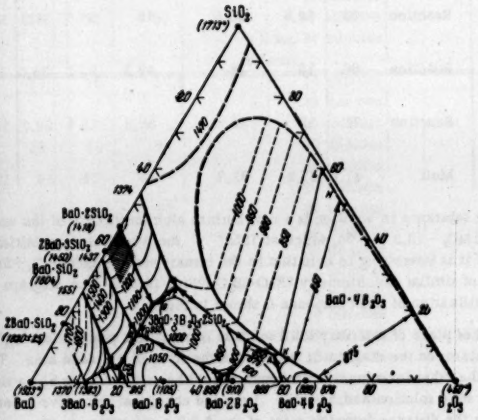

Fig. 5. Phase diagram of the system $BaO - B_2O_3 - SiO_2$.

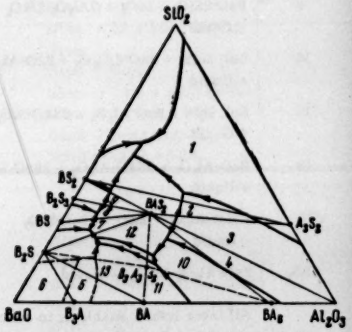

Fig. 7. Phase triangles of the diagram of $BaO - Al_2O_3 - SiO_2$: 1) $SiO_2 - BS_2 - A_2S_3$; 2) $BAS_2 - BS_2 - A_3S_2$; 3) $BAS_2 - A_3S_2 - Al_2O_3$; 4) $BAS_2 - Al_2O_3 - BA_6$; 5) $BS_2 - B_3A - BA$; 6) $B_2S - BaO - B_3A$; 7) $BAS_2 - BS - B_2S$; 8) $BAS_2 - B_2S_3 - BS$; 9) $BAS_2 - BS_2 - B_2S_3$; 10) $BAS_2 - BA_6 - B_3A_3S_2$; 11) $BA - BA_6 - B_3A_3S_2$; 12) $BAS_2 - B_2S - B_3A_3S_2$; 13) $B_2S - BA - B_3A_3S_2$.

TABLE 1

Invariant points of the system $BaO-Al_2O_3-SiO_2$

Points	Phases	Process	Composition						Temperature, °C
			wt. %			mol. %			
			BaO	Al_2O_3	SiO_2	BaO	Al_2O_3	SiO_2	
1	$Al_2O_3 + 3Al_2O_3 \cdot 2SiO_2$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Reaction	28	32	40	15.7	27	57.3	1590
2	$Al_2O_3 + BaO \cdot 6Al_2O_3$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Reaction	41	37	22	26.9	36.4	36.7	1610
3	Sol. soln. + $BaO \cdot 6Al_2O_3$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Reaction	48.5	35	16.5	33.8	36.8	29.4	1580
4	Sol. soln. + $2BaO \cdot SiO_2$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Eutectic	63	14.5	22 5	44 3	15.3	40.4	1330
5	$2BaO \cdot SiO_2$ + $BaO \cdot SiO_2$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Eutectic	64	10	26	44	10 3	45.7	1360
6	$BaO \cdot SiO_2$ + Sol. soln. + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Eutectic	58	10	32	37.5	9 8	52.7	1320
7	Sol. soln. + $BaO \cdot 2SiO_2$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Reaction	49	10	41	29	8 9	62.1	1280
8	$BaO \cdot 2SiO_2 + 3Al_2O_3 \cdot 2SiO_2$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Reaction	37	11	52	19.8	9	71.2	1240
9	$BaO \cdot 2SiO_2 + SiO_2 + 3Al_2O_3 \cdot 2SiO_2$ + liquid	Eutectic	32	11	57	16.4	8.6	75	1230
10	Sol. soln. + $BaO \cdot 6Al_2O_3$ + $BaO \cdot Al_2O_3$ + liquid	Reaction	49	37	14	34.8	39 7	25.5	1610
11	Sol. soln + $BaO \cdot Al_2O_3$ + $2BaO \cdot SiO_2$ + liquid	Reaction	63	16.5	20.5	45	17 7	37.3	1340
12	$BaO \cdot Al_2O_3 + 3BaO \cdot Al_2O_3$ + $2BaO \cdot SiO_2$ + liquid	Reaction	66	18	16	49.3	20 2	30.5	1490
13	$3BaO \cdot Al_2O_3 + BaO$ + $2BaO \cdot SiO_2$ + liquid	Reaction	72	13	15	55.3	15 1	29.6	1520
BAS_2	$BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Melt	41.1	27.2	31.7	25	25	50	1740

All these results enable us to conclude that the substance in question is a new barium aluminosilicate of the composition $3BaO \cdot 3Al_2O_3 \cdot 2SiO_2$ (BaO – 52, Al_2O_3 – 34.5 0 and SiO_2 – 13.5 wt.-%), which at 1550° melts with decomposition into the monoaluminate $BaO \cdot Al_2O_3$ and a liquid. Here it is interesting to note that in the ternary system $BaO-B_2O_3-SiO_2$ was recently established the formation of a compound of similar stoichiometry $3BaO \cdot 3B_2O_3 \cdot 2SiO_2$ [9,12]. The diagram on which can be seen the position of the field of crystallization of this compound is shown in Figure 5.

In the system in question the formation also takes place of a ternary solid solution occupying a position analogous to the position of the ternary solid solution in our system; on the diagram it is shown in the form of a shaded area. The region of the possible existence of the composition of the other incongruent compound should be ascertainable by starting, first, from the position of the field of stability of the solid solution and, second, from the change of refractive index. The light refraction of the solid solution increased with the distance from the point of the 3:3:2 composition in the direction of the $BaO-SiO_2$ side of the triangle. Attempts to find the other ternary compound in the indicated direction were, however, unsuccessful. The probable second component of the solid solution may be regarded as barium metasilicate, judging by the character of the arrangement of the field and the change in the refractive index of the solid solution.

A photomicrograph of a polished section (Fig. 6.) illustrates the crystal form of this new phase; it is made up of elongated prisms with right extinction interlacing and mutually intergrowing at various angles. The interstices between the crystals are filled with glass and with secondary segregations of celsian. The light refraction fluctuates within the following limits: Ng = 1.624 – 1.644 and Np = 1.615 – 1.632.

TABLE 2

Sequence of separation of crystalline phases in the region of the solid solution of the incongruent compound $3Ba_2O \cdot 3Al_2O_3 \cdot 2SiO_2$

Composition in wt. %			Conditions		Phases
BaO	Al_2O_3	SiO_2	Duration	Temp. in deg. C.	
1	2	3	4	5	6
62.5	15	22.5	2 hours, 30 minutes	1350	Glass
			2 hours, 30 minutes	1300	Glass + BAS_2
			1 hour, 40 minutes	1200	Glass + BAS_2 + B_2S
63	16	21	1 hour,	1350	Glass
			1 hour	1300	Glass + B_2S
			1 hour	1200	Glass + B_2S + BAS_2
60	17.5	22.5	2 hours	1350	Glass
			1 hour, 15 minutes	1300	Glass + Sol, soln,
			2 hours	1250	Glass + solid solution + BAS_2
62.5	17.5	20	2 hours	1360	Glass
			2 hours	1300	Glass + BA + solid solution
62.5	20	17.5	20 minutes	1450	Glass
			30 minutes	1400	Glass + BA
			40 minutes	1250	Glass + BA + B_2S
60	20	20	60 minutes	1400	Glass
			2 hours	1360	Glass + solid solution
			1 hour, 30 minutes	1200	Glass + solid solution + B_2S
57	20	23	30 minutes	1430	Glass
			30 minutes	1350	Glass + BAS_2
			3 hours, 30 minutes	1300	Glass + BAS_2 + solid solution
60	22.5	17.5	15 minutes	1600	Glass
			20 minutes	1580	Glass + BA
			2 hours, 15 minutes	1350	Glass + BA + solid solution
54.7	24	21.3	30 minutes	1450	Glass
			30 minutes	1400	Glass + BAS_2
			20 minutes	1350	Glass + BAS_2 + solid solution
55	25	20	40 minutes	1420	Glass
			1 hour, 30 minutes	1380	Glass + solid solution
			6 hours	1250	Solid solution + BAS_2
57.5	25	17.5	15 minutes	1600	Glass
			30 minutes	1550	Glass + BA
			30 minutes	1400	Glass + BA + solid solution
52	28	20	30 minutes	1500	Glass
			30 minutes	1470	Glass + BAS_2
			20 minutes	1400	Glass + BAS_2 + solid solution
53	30	17	30 minutes	1550	Glass
			30 minutes	1530	Glass + BA
			30 minutes	1500	Glass + BA + solid solution
48.7	32.3	19	15 minutes	1600	Glass
			30 minutes	1550	Glass + BAS_2
			10 minutes	1490	Glass + BAS_2 + solid solution
50	33	17	20 minutes	1600	Glass
			10 minutes	1560	Glass + solid solution
			10 minutes	1530	Glass + solid solution + BAS_2
50	35	15	30 minutes	1600	Glass
			30 minutes	1550	Glass + solid solution
			25 minutes	1500	Glass + solid solution + BAS_2
51.9	34.6	13.5	15 minutes	1600	Glass + BA
			40 minutes	1050	Solid solution
47.5	35	17.5	15 minutes	1600	Glass
			40 minutes	1550	Glass + BAS_2
			60 minutes	1500	Glass + BAS_2 + BA_6
45.5	37	17.5	15 minutes	1600	Glass + BA_6 + BAS_2

(continued on following page)

TABLE 2 (cont.)

1	2	3	4	5	6
48	36	16	15 minutes	1600	Glass + BA_6
			40 minutes	1550	Glass + BA_6 + solid solution
48,5	36,5	15	15 minutes	1600	Glass
			40 minutes	1550	Glass + solid solution
			60 minutes	1500	Glass + solid solution + BA_6 + BAS_2
47	40	13	20 minutes	1600	Glass + BA_6
			40 minutes	1550	Glass + BA_6 + solid solution
49	37	14	15 minutes	1600	Glass + BA_6
			40 minutes	1550	Glass + BA_6 + solid solution
50	37	13	15 minutes	1600	Glass + solid solution + BA

The course of crystallization in the region of this solution and of the adjacent fields is clarified by the data of Table 2, in which the sequence of separation of the crystalline phases is shown. The boundary with the monoaluminate field is incongruent in character; the boundary with the celsian field is eutectic in character. The division of the whole diagram into phase triangles is shown in Figure 7. This enables speedy establishment of the final products of crystallization of the various compositions in the system. Triangle 9 is a two-phase one since one of the sides represents solid solutions. Triangles 10 to 13 are distinguished in the diagram by a broken line because one of the phases ($B_3A_3S_2$) melts with decomposition.

Technological Application

Prominent in the region of glassy compositions of the diagram is the zone located in the "valley" bordering on the curve between the $BaO \cdot 2SiO_2$ and $3Al_2O_3 \cdot 2SiO_2$ fields (Fig.1), which may present interest for glass technology. The glasses of this zone, as far as one can judge from the data obtained in the present investigation, combine valuable industrial and technical qualities. They are relatively low-melting (liquidus temperature approx. 1200°) and are difficultly crystallizable, and they have lower silica contents and higher chemical stability. All these characteristics suggest the possibility of obtaining valuable technical glasses by blending the components of the system in the indicated region with other oxides.

The high quality of celsian ceramic products is well known. The recommended compositions of such products [13] are extremely interesting. They were derived from technical tests of various compositions on the basis of the oxides of the system in question: BaO from 31 to 51%; Al_2O_3 from 17 to 37%; SiO_2 from 22 to 42%. It appears that these values precisely mark the region of the diagram in which the whole of the field of stability of celsian is located. The application of the diagram to the development of recipes and procedures for firing may lead to further advances in the improvement of the quality of celsian products.

SUMMARY

1. An investigation established the congruence of melting of mullite, and the appropriate corrections were introduced into the phase diagram of the system $Al_2O_3-SiO_2$.

2. The phase diagram of the system $BaO-Al_2O_3-SiO_2$ was studied; it comprises 13 fields of stability of the various phases.

3. In the system is formed a ternary solid solution between the silicates $2BaO \cdot 3SiO_2$ and $BaO \cdot 2SiO_2$ and the aluminosilicate $BaO \cdot Al_2O_3 \cdot 2SiO_2$.

4. Formation of a previously unknown aluminosilicate of the composition $3BaO \cdot 3Al_2O_3 \cdot 2SiO_2$ was observed. This compound melts with decomposition into the monoaluminate $BaO \cdot Al_2O_3$ and a liquid.

5. A new high-temperature micro-furnace was designed.

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Received April 1, 1954

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STUDY OF SYSTEMS CONTAINING CONCENTRATED HYDROGEN PEROXIDE

COMMUNICATION 6. 0 AND 20° ISOTHERMS OF THE TERNARY SYSTEM $Mg(OH)_2 - H_2O_2 - H_2O$

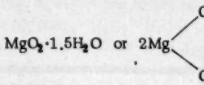
S. Z. Makarov and I. I. Volnov

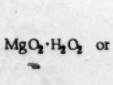
Products known by the names of "heavy", "semiheavy", "light" magnesium peroxide, containing from 12 to 50% MgO_2, are supplied by the chemical industry for pharmaceutical purposes, as an activator in the vulcanization of synthetic rubber, and as a bleaching agent in the textile industry. By a preparative method (in the main by interaction of magnesia with hydrogen peroxide) various authors [1-7] have obtained 19 magnesium products containing MgO_2 which are regarded as a mixture of MgO and MgO_2, $Mg(OH)_2$ and MgO_2, as molecular compounds of MgO and H_2O_2, as basic hydroperoxides of the gross composition , and as products of sorption of H_2O_2 on magnesia. The lack of systematic investigations based upon the methods of physicochemical analysis is a main cause of the discrepancies in the results obtained.

For determination of the character of the possible forms of the peroxy compounds of magnesium, we plotted on the Gibbs phase diagram of $MgO - H_2O - 0.5O_2$ (Fig. 1) the compositions of 19 products mentioned in the literature, the figurative points of the main compounds involving H_2O, H_2O_2, MgO, MgO_2 and $Mg(OH)_2$ and of the hypothetical compounds $2MgO \cdot MgO_2$ and $MgO \cdot 4MgO_2$ for which the existence of hydrates may be possible.

Examination of the diagram shows that of the 19 magnesium compounds reported in the literature, specific chemical compounds can only be associated with the figurative points corresponding to the compositions:

MgO_2; $MgO_2 \cdot 2H_2O$ or $Mg(OH)_2 \cdot H_2O_2$ or ;

 ; $MgO_2 \cdot H_2O$ or $MgO \cdot H_2O_2$ or ;

 ;

the remaining products may be regarded as mixtures.

The best method of approaching the problem of the composition of the products possible as a result of interaction of MgO or $Mg(OH)_2$ with H_2O_2 solutions will evidently be a systematic study of the equilibria in the ternary system $Mg(OH)_2 - H_2O_2 - H_2O$ by the solubility method and by a special physicochemical study of the solid phases of this system.

EXPERIMENTAL

Procedure. In the investigation of the system $Mg(OH)_2 - H_2O_2 - H_2O$ we used solutions of chemically pure H_2O_2 (without inhibitor) of 1.5 to 97% concentration and chemically pure magnesia (Merck). According to the label the MgO contained the following impurities: Cl' 0.00%; PO_4''' 0.0006%; SO_4'' 0.00%; Pb'' 0.001%; Fe''' 0.0005%.

The magnesia was calcined at 800° to constant weight for complete elimination of CO_2 since $MgCO_3$ dissociates in the 600-800° range; it was then slaked by Feitknecht's method [8] for 48 hours with a hundredfold excess of distilled water previously thoroughly boiled with stirring and periodic heating to 90°. Analysis showed that slaking was complete since after drying to constant weight at 115° the product contained 30.87% H_2O [$Mg(OH)_2$ contains 30.86% H_2O]. Water of constitution was determined by calcining at 500-550° since $Mg(OH)_2$ dissociates completely at 410°. After slaking, the liquid phase was decanted. The suspension of $Mg(OH)_2$ contained on the average 80% H_2O. The solubility vessel containing the $Mg(OH)_2$ suspension was placed

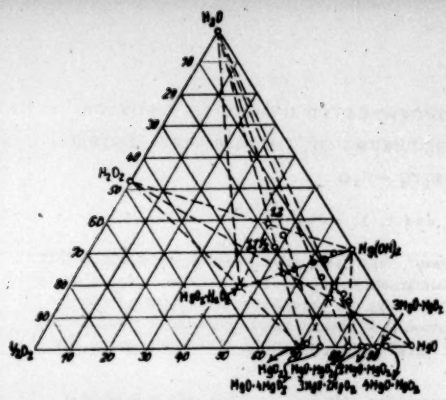


Fig. 1. Compositions of peroxy compounds of magnesium according to literature data in the Gibbs phase diagram.

in an ice-filled cryostat and, after cooling, a definite volume of H_2O_2 solution of increasing concentration was added for each of the "points" to be determined in such a manner that the excess of H_2O_2 ranged from 1.5 to 150 of the stoichiometric amount. The time established for attainment of equilibrium did not exceed 3 hours. The composition of the solid phases was established by the residue method (plotting on the Gibbs phase diagram the analytical data for the liquid phases and residues). The active oxygen in the residues was determined by titration with 0.1 N $KMnO_4$, and the Mg^{++} ion in the form of $Mg_2P_2O_7$. In the liquid phase the active oxygen was likewise determined by titration with 0.1 N $KMnO_4$, but the Mg^{++} ion, due to the poor solubility of $Mg(OH)_2$ – of the order of 10^{-4} mole/liter was determined colorimetrically, after complete decomposition of the H_2O_2, with the help of titanium yellow indicator using Kolthoff's method [9] and a FEK-1 electrophotocolorimeter.

Solubility data for the 0 ° isotherm of the system $Mg(OH)_2 - H_2O_2 - H_2O$: The solubility data for the 0 ° isotherm of the system $Mg(OH)_2 - H_2O_2 - H_2O$ are presented in Table 1 and Figure 2.

As we see from Fig. 2, at least 3 solid phases are stable at 0 deg: $Mg(OH)_2$ in the range from 0 to 1.5 % H_2O_2; $MgO_2 \cdot H_2O$ in the range from 1.5 to 62% H_2O_2 and MgO; and $MgO_2 \cdot \frac{1}{2} H_2O$ in the range from 62 to 97% H_2O_2. Anhydrous magnesium peroxide is not formed at the temperature in question.

TABLE 1

Point Number	Liquid Phase		Residue		Solid phase
	wt. % MgO	wt. % 1/2 O_2	wt. %	wt. % 1/2 O_2	
1	0.002	—	—	—	$Mg(OH)_2$
15	0.05	0.43	25.48	8.50	$Mg(OH)_2$ + $MgO_2 \cdot H_2O$
8	0.02	0.62	21.12	8.48	$MgO_2 \cdot H_2O$
9	—	6.02	19.61	11.60	ditto
16	0.01	6.37	20.86	13.51	ditto
7	0.02	9.04	—	—	ditto
3	0.03	15.47	—	—	
20	0.10	16.02	25.70	20.60	ditto
12	0.14	27.83	16.82	26.22	ditto
11	0.13	28.45	16.20	26.66	ditto
5	0.10	33.61	20.10	30.48	$MgO_2 \cdot 0.5H_2O$
13	0.04	38.99	14.63	35.10	ditto
17	—	43.35	14.12	39.54	ditto
14	—	44.45	16.67	38.36	ditto
19	—	45.06	25.73	36.11	ditto
18	—	45.25	22.49	36.92	ditto

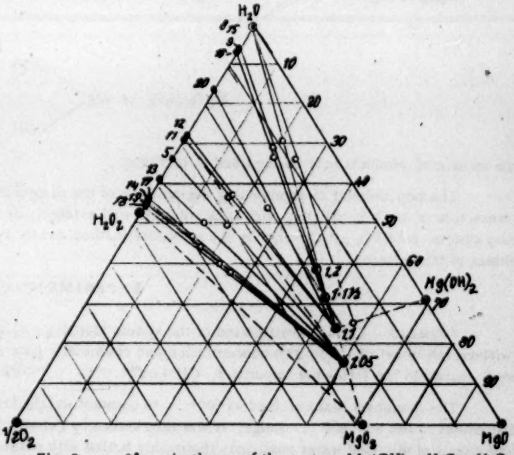


Fig. 2. 0° isotherm of the system $Mg(OH)_2 - H_2O_2 - H_2O$ in triangular coordinates.

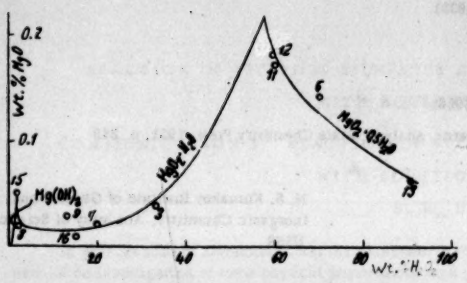


Fig. 3. 0° isotherm of the system $Mg(OH)_2-H_2O_2-H_2O$ in triangular coordinates.

Special interest attaches to the solubility isotherm (Fig. 3), plotted from data for colorimetric determination of magnesium in the liquid phase. The transition points of $Mg(OH)_2 + MgO_2 \cdot H_2O$ and $MgO_2 \cdot H_2O + MgO_2 \cdot 0.5H_2O$ correspond to conspicuous maxima which indicate the possibility of complex formation and point to definite limits to the existence of the corresponding solid phases. In comparison with water, the solubility of $Mg(OH)_2$ in which is 0.002 wt.% in H_2O_2 solutions the solubility increases 10 times (point 8) and even 50-75 times (points 20 and 12).

20° solubility isotherm of the system $MgOH_2-H_2O_2-H_2O$. Data for the +20° isotherm of this system are set forth in Table 2 and plotted on the phase diagram (Fig. 4. As we see from Fig. 4, at 20° the solubility isotherm of the system $Mg(OH)_2-H_2O_2-H_2O$ is characterized by the presence of three solid phases: $Mg(OH)_2$ in the H_2O_2 concentration range of 0 to 2%; $MgO_2 \cdot 0.5H_2O$ in the H_2O_2 concentration range of 2 to 30%; and anhydrous magnesium peroxide in the H_2O_2 concentration range of 30 to 62%. Above this concentration equilibrium is not attained due to progressive decomposition of H_2O_2.

TABLE 2

Point Number	Liquid phase wt.% $0.5O_2$	Residue wt. % $0.5\ O_2$	Residue wt. % MgO	Solid phase
12	0,55	0,55	35,20	$Mg(OH)_2$
10	0,80	12,90	32,10	$MgO_2 \cdot 0.5H_2O$
9	1,20	13,10	31,00	ditto
8	2,41	14,10	30,70	ditto
7	3,27	14,10	28,20	ditto
6	4,65	14,90	29,30	ditto
5	8,37	16,04	28,48	ditto
1	10,30	17,40	28,94	ditto
2	13,84	20,73	29,16	MgO_2
11	22,30	25,03	32,34	ditto
3	29,14	28,61	27,40	ditto
4	40,43	33,73	23,81	

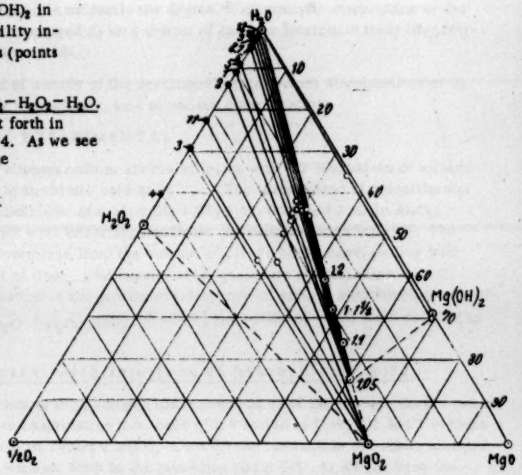


Fig. 4. 20 ° isotherm of the system $Mg(OH)_2-H_2O_2-H_2O$

SUMMARY

Investigation of the ternary system $Mg(OH)_2-H_2O_2-H_2O$ at 0° and at +20° by the solubility method over a wide range of concentrations of H_2O_2 established the possibility of existence of three individual peroxy compounds of magnesium with the compositions: MgO_2; $MgO_2 \cdot 0.5H_2O$ and $MgO_2 \cdot H_2O$.

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Received November 26, 1953

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REACTION OF VITREOUS SILICATES AND SODIUM ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

COMMUNICATION 4. REACTION OF VITREOUS SODIUM ALUMINOSILICATES WITH SOLUTIONS OF ACIDS

S. K. Dubrovo

In vitreous sodium aluminosilicates the aluminum is structurally analogous to silicon, as was established on the basis of an investigation of some physical properties of such glasses [1]. Nevertheless, on comparing the behavior in acid solutions of sodium silicates and the corresponding aluminosilicates, characteristic features of the presence of the aluminum ion in the glass are manifested. Evidently Sobolev's observation (to the effect that aluminosilicates, regardless of the isostructural position of the silicon and aluminum, must be regarded as double salts from the chemical standpoint) is valid [2].

In our preceding paper, on the basis of experimental data, a mechanism was advanced for the decomposition of sodium aluminosilicates by solutions of acids which involved as an initial stage a process of exchange of ions of sodium and aluminum by the hydrogen ions of the solution [3]. We should then expect the rate of decomposition of sodium aluminosilicates to be governed mainly, on the one hand, by the hydrogen ion concentration of the solution and, on the other hand, by the nature and state of the resultant products of decomposition both in solution and on the surface of the glass. The essential factor is evidently the degree of electrolytic dissociation of the salts formed in solution. From this standpoint it appeared to be a matter of extreme interest to study the interaction of aluminosilicates with solutions of various acids.

In the present paper results are submitted of a study of the decomposition of sodium aluminosilicates by solutions of sulfuric and nitric acids and also by hydrochloric acid of various concentrations.

EXPERIMENTAL

We studied the interaction of a series of vitreous sodium aluminosilicates with 0.1 N solutions of sulfuric and nitric acids, and also with 0.01 N and 1 N hydrochloric acid at 40°. The investigated aluminosilicates belonged to the sodium disilicate series with admixtures of 0.15; 0.25; 0.30; 0.40; 0.50 and 1 mole Al_2O_3. Melting of the glasses and preparation of samples were undertaken as in the previous investigations [4]. The decomposability of the aluminosilicates was determined from the amount of all the components passing from the glass into solution after a specified interval of time. The experimental procedure was the same as that previously employed by us [3]. For characterization of the process of interaction of sodium aluminosilicates with acid solutions, we used the magnitudes of n_{Na_2O}, $n_{Al_2O_3}$, n_{SiO_2}, β and α, the values of which were detailed in the preceding paper [3].

Interaction of sodium aluminosilicates with solutions of hydrochloric acid

With the objective of studying the influence of the hydrogen ion concentration of the solution on the course of decomposition of sodium aluminosilicates, an examination was made of the action of 0.01, 0.1 and 1 N hydrochloric acid solutions. These results are set forth in Tables 1 and 2. Data for the interaction of sodium aluminosilicates with 0.1 N hydrochloric acid solution were set forth in the preceding paper [3]. As we see from the data of Table 1, which show the decomposability of aluminosilicates in 0.01 N hydrochloric acid solution, admixtures with the sodium disilicate of 0.15 and 0.30 mole Al_2O_3 sharply reduce the amounts of Na_2O passing into solution from the glass in comparison with what happens in the case of the disilicate. This represents the lowest degree of decomposition. However, the degree of decomposition of the residual aluminosilicate layer increases with increasing Al_2O_3 content of the glasses, as reflected in an increase in the values of β and α. But whereas for the glass with admixture of 0.15 mole Al_2O_3 the values of β and α are extremely small and equal to one another, for the glass containing 0.3 mole Al_2O_3 there is substantially complete washing out of the aluminum ions from the decomposed layer. The amount of SiO_2 passing into solution, however, remains relatively very small (6-8%).

When the Al_2O_3 admixture to the sodium disilicate is increased to 0.4 mole, this glass suffers intensive decomposition: the quantities of all components passing into solution increase sharply, the amount of silica transferred being approximately 40% of its content in the residual layer ($\alpha = 0.4$). After treatment of the samples of glass of the composition $Na_2O \cdot 0.4Al_2O_3 \cdot 2SiO_2$ with 0.01 N hydrochloric acid solution and drying at 40°.

TABLE 1

Interaction of sodium aluminosilicates with 0.01 N hydrochloric acid solution at 40°

Molar ratio			moles / cm² · 10⁻⁶	Duration in hours				
Na_2O	Al_2O_3	SiO_2		1	2	4	6	8
1	0.15	2	n_{Na_2O}	1.8	2.7	4.0	4.9	5.5
			$n_{Al_2O_3}$	–	–	–	–	0.004
			n_{SiO_2}	–	–	–	–	0.03
			β	–	–	–	–	0.004
			α	–	–	–	–	0.003
1	0.30	2	n_{Na_2O}	1.9	2.1	2.2	2.4	2.3
			$n_{Al_2O_3}$	0.7	0.8	0.8	0.7	0.7
			n_{SiO_2}	0.3	0.3	0.3	0.3	0.4
			β	1.2	1.2	1.2	0.97	1.0
			α	0.08	0.07	0.07	0.06	0.08
1	0.40	2	n_{Na_2O}	7.9	15.0	24.0	25.0	28.0
			$n_{Al_2O_3}$	3.1	6.0	8.3	8.9	9.3
			n_{SiO_2}	7.0	13.0	19.0	20	20
			β	0.98	0.97	0.85	0.88	0.85
			α	0.44	0.43	0.40	0.40	0.36
1	0.5	2	n_{Na_2O}	3.0	7.2	16.0	21	22
			$n_{Al_2O_3}$	1.5	3.2	6.7	8.9	9.3
			n_{SiO_2}	6.2	13.6	29.0	38.0	41.0
			β	1	0.90	0.85	0.85	0.85
			α	1	0.94	0.90	0.93	0.93
1	0	2	n_{Na_2O}	–	–	68	88	104
			n_{SiO_2}	–	–	0.4	1.1	2.0
			α	–	–	0.003	0.006	0.010

on their surface was observed a crumbly, friable layer. Chemical analysis of this residual layer revealed a content of approx. 96% SiO_2.

Subsequent addition of Al_2O_3 up to 0.5 mole leads to a certain drop in the amount of Na_2O passing into solution and consequently to a fall in the depth of the decomposed layer of glass in comparison with the glass of the composition $Na_2O \cdot 0.4Al_2O_3 \cdot 2SiO_2$. On the other hand, the relative amount of SiO_2 passing into solution from the residual layer increases: the value of α rises to 0.93; that of β to a little less. Possibly this is bound up with reverse adsorption by the surface of the glass of the aluminum ions passing into solution. Consequently the residual aluminosilicate layer is almost completely decomposed.

The data of Table 2 characterize the decomposability of sodium aluminosilicates in 1 N hydrochloric acid solution. They show that the first Al_2O_3 additions of 0.15 and 0.25 mole to the disilicate sharply reduce the quantity of Na_2O passing into solution. Simultaneously, starting from the composition $Na_2O \cdot 0.25Al_2O_3 \cdot 2SiO_2$, the decomposition of the aluminosilicate skeleton is intensified in the direction of preferential washing-out of aluminum ions. Unlike

TABLE 2

Interaction of sodium aluminosilicates with 1 N hydrochloric acid solution at 40°

Molar ratio			moles $\frac{\text{moles}}{\text{cm}^3} 10^{-6}$	Duration in hours				
Na_2O	Al_2O_3	SiO_2		1	2	4	6	8
1	0.15	2	n_{Na_2O}	2.1	2.8	3.8	3.9	4.9
			$n_{Al_2O_3}$	–	–	–	–	–
			n_{SiO_2}	–	–	–	–	–
			β	–	–	–	–	–
			α	–	–	–	–	–
1	0.25	2	n_{Na_2O}	1.2	1.4	1.9	2.3	2.4
			$n_{Al_2O_3}$	0.21	0.21	0.19	0.19	0.19
			n_{SiO_2}	0.03	0.07	0.14	0.14	0.21
			β	0.07	0.60	0.40	0.33	0.32
			α	0.012	0.025	0.036	0.030	0.043
1	0.30	2	n_{Na_2O}	11	31	68	92	133
			$n_{Al_2O_3}$	3.7	7.5	15.0	24.0	31.0
			n_{SiO_2}	1.4	2.0	3.6	6.0	7.9
			β	1.1	0.80	0.75	0.86	0.77
			α	0.064	0.032	0.029	0.032	0.030
1	0.40	2	n_{Na_2O}	69.2	141	300	442	603
			$n_{Al_2O_3}$	29.2	57.2	115	176	240
			n_{SiO_2}	59	74-118	125-183	164-247	292
			β	1.05	1.01	0.96	1.0	1.0
			α	0.42	0.37-0.42	0.20-0.30	0.20-0.28	0.24
1	0.50	2	n_{Na_2O}	69	148	336	573	830
			$n_{Al_2O_3}$	37	80	163	255	350
			n_{SiO_2}	136	300	612	962	1232
			β	1.01	1.08	0.91	0.89	0.84
			α	0.99	1.01	0.91	0.84	0.70
1	1	2	n_{Na_2O}	–	67	160	219	307
			$n_{Al_2O_3}$	–	70	153	208	298
			n_{SiO_2}	–	138	273	450	592
			β	–	1.04	0.95	0.95	0.97
			α	–	1.03	0.89	1.02	0.96
1	0	2	n_{Na_2O}	25.3	41	64	88	105
			n_{SiO_2}	0	0	0	0	0

the action of weaker solutions of hydrochloric acid (0.01 and 0.1 N) a sharp rise in the amount of Na_2O going into solution commences even with a composition containing 0.3 mole Al_2O_3.

TABLE 3

Reaction of sodium aluminates with 0.1 N sulfuric and hydrochloric acid solutions at 40°

Molar ratio			moles $\frac{}{cm^2} 10^{-6}$	Duration in hours					Acid
Na_2O	Al_2O_3	SiO_2		1	2	4	6	8	
1	0.15	2	n_{Na_2O}	2.6	3.8	4.3	5.1	6.8	
			$n_{Al_2O_3}$	—	—	—	0	0	
			n_{SiO_2}	—	—	—	0	0	
			ß	—	—	—	0	0	0.1 N
			α	—	—	—	0	0	H_2SO_4
1	0.15	2	n_{Na_2O}	1.7	2.4	3.7	4.3	4.7	
			$n_{Al_2O_3}$	—	—	—	0.014	0.016	
			n_{SiO_2}	—	—	—	0.010	0.014	0.1 N
			ß	—	—	—	0.02	0.02	HNO_3
			α	—	—	—	0.001	0.002	
1	0.30	2	n_{Na_2O}	4.4	8.4	12	14	14	
			$n_{Al_2O_3}$	1.5	2.3	3.1	3.6	3.7	
			n_{SiO_2}	0.5	0.8	1.2	1.4	1.6	0.1 N
			ß	1.1	0.90	0.83	0.86	0.91	H_2SO_4
			α	0.056	0.047	0.048	0.050	0.051	
1	0.40	2	n_{Na_2O}	29	58	108	145	174	
			$n_{Al_2O_3}$	12	24	43	55	68	
			n_{SiO_2}	29	59	121	140	176	0.1 N
			ß	1.03	1.03	1.0	0.95	0.99	H_2SO_4
			α	0.50	0.51	0.54	0.48	0.51	
1	0.40	2	n_{Na_2O}	13	26	55	87	119	
			$n_{Al_2O_3}$	5.0	9.6	22	32	44	
			n_{SiO_2}	20	32	57	83	95	0.1 N
			ß	0.96	0.92	1.0	0.92	0.97	HNO_3
			α	0.77	0.61	0.52	0.48	0.40	
1	0.50	2	n_{Na_2O}	36	81	146	175	201	
			$n_{Al_2O_3}$	18	37	69	82	87	
			n_{SiO_2}	76	152	275	335	369	0.1 N
			ß	1	0.91	0.95	0.93	0.87	H_2SO_4
			α	0.05	0.94	0.94	0.96	0.92	

TABLE 3 (cont.)

Molar ratio			moles / cm² · 10⁻⁶	Duration in hours					Acid
Na_2O	Al_2O_3	SiO_2		1	2	4	6	8	
1	0,50	2	n_{Na_2O}	9,8	22	46	75	92	
			$n_{Al_2O_3}$	5,1	10	23	33	45	
			n_{SiO_2}	21	43	88	135	186	0,1 N
			β	1,04	0,93	1,0	0,90	0,98	HNO_3
			α	1,06	0,97	0,96	0,90	1,01	
1	1	2	n_{Na_2O}	16	37	76	120	153	
			$n_{Al_2O_3}$	14	25	66	106	144	
			n_{SiO_2}	29	65	148	217	278	0,1 N
			β	0,83	0,70	0,86	0,81	0,94	H_2SO_4
			α	0,90	0,87	0,98	0,90	0,91	
1	0	2	n_{Na_2O}	26	52	74	94	119	
			n_{SiO_2}	0,05	0,04	0,14	0,23	0,60	0,1 N
			α	0,001	0,0004	0,0010	0,0010	0,003	H_2SO_4

Further additions of 0,4 and 0,5 mole Al_2O_3 intensify the decomposability of the glasses, the absolute amounts of all components passing into solution being increased. During this process the Al_2O_3 is completely washed out from the residual layer of the glass of composition $Na_2O{\cdot}0,4Al_2O_3{\cdot}2SiO_2$. The quantities of SiO_2 passing into solution, however, amounted at the start to approximately 40% of its content in the residual layer (as in the action of less concentrated acids), after which these amounts progressively decreased. Addition of 0,5 mole Al_2O_3 to sodium disilicate leads to a further increase in the amounts of all components passing into solution, while the ratio of Al_2O_3 and SiO_2 in the solution is substantially equal to their original ratio in the starting glass. A process of dissolution, as it were, of the glass of composition $Na_2O{\cdot}0.5Al_2O_3{\cdot}2SiO_2$ in 1 N hydrochloric acid takes place, as was the case in the action of an 0,1 N solution of the same acid. With passage of time, however, as we see from Table 2, α and β decrease. This must evidently be the result of a secondary process of partial coagulation, at the surface of the glass, of the silica which had accumulated in the solution and whose concentration in the experimental conditions reached 0,01 g/ml. The coagulating silica could adsorb aluminum ions. The later increase to 1 mole of the Al_2O_3 content of the sodium aluminosilicate results in a drop in the absolute amounts of components going into solution, although the character of the decomposition remains essentially the same as when 0.5 mole Al_2O_3 had been added.

Interaction of sodium aluminosilicates with solutions of sulfuric and nitric acids

In Table 3 are set forth the results of a determination of the decomposability of sodium aluminosilicates in 0,1 N solutions of sulfuric and nitric acids. As is evident from the data for all the three aluminosilicates investigated, the amounts of components going into solution on interaction with 0,1 N solution of nitric acid are approximately the same as on interaction with hydrochloric acid of the same concentration. The action of 0,1 N sulfuric acid solution on all the investigated aluminosilicates is considerably more intensive than that of hydrochloric and nitric acids, although the character of the decomposition remains identical over the range of compositions studied. The decomposition of the aluminosilicate skeleton likewise proceeds in the direction of preferential removal of aluminum ions. The relative amounts of SiO_2 passing into solution thus increase with increasing content of Al_2O_3 in the composition of the investigated glasses. For the composition $Na_2O{\cdot}0,5Al_2O_3{\cdot}2SiO_2$ passage into solution of the Al_2O_3 and SiO_2 takes place in the same ratios as those which were present in the original glass, and this occurred in the case of both hydrochloric and nitric acid. A fall in the degree of decomposition of sodium aluminosilicates in 0,1 N sulfuric acid solution is observed in passing from a composition containing 0,5 mole Al_2O_3 to a composition to which 1 mole Al_2O_3 was added. In contrast to what happens in treatment with 0,1 N

TABLE 4

Amount of molecularly dispersed silica in the samples in %

Molar ratio			Acid used	Duration of action (hours)	SiO_2 conc. ($g/ml \cdot 10^{-4}$)	Amount of molecularly dispersed silica in % of its total content in the solution
Na_2O	Al_2O_3	SiO_2				
1	0,3	2	1 N HCl	6	0,62	98
1	0,3	2	1 N HCl	8	0,58	95
1	0,4	2	0,01 N HCl	8	1,2	94
1	0,5	2	ditto	6	2,4	72
1	0,5	2	ditto	8	2,2	76
1	0	1,7	0,1 N HCl	3	2,6	52
1	0	1,7	ditto	4	6,3	47
1	0,5	2	ditto	6	8,1	66
1	0,5	2	ditto	8	11,4	66
1	0,4	2	1 N HCl	6	19	53
1	0,5	2	0,1 N H_2SO_4	6	20	78
1	0,5	2	0,1 N H_2SO_4	8	22,0	73
1	0,4	2	1 N HCl	8	25,5	35

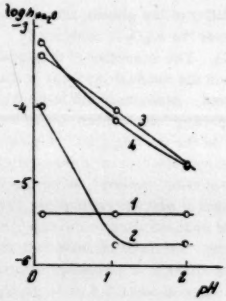

Fig. 1. Dependence of leaching out of Na_2O on the pH of the reacting solution of hydrochloric acid: 1) glass with the composition $Na_2O \cdot 0,15Al_2O_3 \cdot 2SiO_2$; 2) glass with composition $Na_2O \cdot 0,30Al_2O_3 \cdot 2SiO_2$; 3) glass with composition $Na_2O \cdot 0,40Al_2O_3 \cdot 2SiO_2$; 4) glass with composition $Na_2O \cdot 0,50Al_2O_3 \cdot 2SiO_2$.

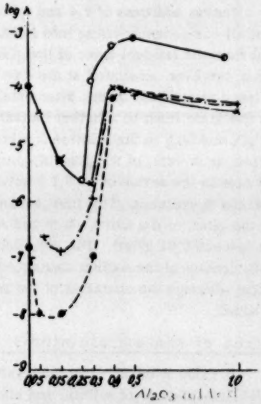

Fig. 2. Dependence of decomposability of sodium aluminosilicates in acids of various concentrations on the Al_2O_3 content: o) $\log n_{Na_2O}$ 1N HCl; x) $\log n_{Na_2O}$, 0,1 N HCl; +) $-\log \frac{n_{Al_2O_3}}{k}$, 0,1 N HCl; •) $-\log \frac{n_{SiO_2}}{2}$, 0,1 N HCl

hydrochloric acid, an 0,1 N sulfuric acid solution increases the amount of Na_2O going into solution on passing from a composition with addition of 0,15 mole Al_2O_3 to one with 0,30 mole Al_2O_3. In this respect 0,1 N sulfuric acid occupies a position intermediate between 0,1 and 1 N hydrochloric acid solutions.

State of the silica passing into solution

In the colorimetric determination of the silica passing into solution from the investigated glasses on the basis of the yellow silicomolybdate complex, we applied in all cases a preliminary "resuscitation" of the SiO_2 by boiling with 1 N NaOH solution, since silicic acid in acidic solutions has a tendency to polymerize. As we know, however, polymerized silicic acid to a considerable extent is not determined colorimetrically [5]. In a parallel series of experiments we also carried out determinations of SiO_2 without preliminary resuscitation. This gave us the possibility of establishing how much silica is present at a given instant in the molecular state in the sample; this knowledge facilitated clarification of the character of the interaction of sodium aluminosilicates with solutions of acids.

In Table 4 are set forth the data for determination of the content of molecularly dispersed silica in the individual samples. We see from these data that the quantities of molecularly dispersed silica in the solution vary in our experiments from 35 to 98% of its total content. The very fact of the presence in the solution of colorimetrically determinable silica is proof that the silica passing into solution is close to the molecularly dispersed state.

Subsequently the polymerization of the silicic acid proceeds with varying velocity in dependence on the concentration of silicic acid in solution, on the character and concentration of the acid acting on the glass, and on the duration of the reaction.

Interest attaches to the fact that when using 0.1 N sulfuric acid the content of molecularly dispersed silica in the solution is higher than when using 0.1 N hydrochloric acid, notwithstanding that in the first case the total SiO_2 concentration is twice as high (see Table 4). This may be explained by the lower activity of sulfuric acid, due to which the silicic acid polymerizes more slowly.

Evaluation of Results

The hydrogen ion concentration of the reacting medium is one of the fundamental factors influencing the rate of decomposition of sodium aluminosilicates. A series of other factors which come into play during the process may, however, mask the influence of the change of hydrogen ion concentration. Such factors are a residual layer on the surface of the glasses which regulates the diffusion of ions, the degree of dissociation of the salts formed in solution, etc.

In Figure 1 is plotted the logarithmic dependence on the pH of the hydrochloric acid solutions of the amounts of Na_2O leached out of the glasses. This diagram shows that increase of hydrogen ion concentration is accompanied by intensified decomposition of the aluminosilicate glasses containing relatively large amounts of Al_2O_3, the skeleton of these glasses, due to depolymerization of the contained silica, being unstable toward acidic solutions. And on the surface of such aluminosilicates, as we have seen, either no residual surface layer is formed or this layer is a crumbly and weakly attached hydrated silica. In such cases the decomposability will be mainly governed by the hydrogen ion concentration when using one and the same acid in various concentrations.

In the case of aluminosilicates containing an addition of up to 0.3 mole Al_2O_3 to the disilicate, a change of hydrogen ion concentration in the acidic region has substantially no effect on their speed of decomposition. The same observation is made in the case of sodium silicates [4]. This phenomenon may be explained in the following way (by analogy with the case of silicates [6]). Due to the formation on the surface of these aluminosilicates of a protective residual aluminosilicate film on reaction with solutions of hydrochloric acid, a masking factor comes into play in the form of diffusion of the exchanging ions through this film. The velocity of diffusion of the sodium ions is governed, however, by their concentration difference in this film. When using acids at the limits of the above-indicated values of pH, the concentration of sodium ions in the residual film at the boundary with the solution is close to zero. Hence the difference of concentrations of the sodium ions in the surface film is at a maximum and is substantially independent of the hydrogen ion concentration.

In Figure 2 is plotted the dependence of the logarithm of the amounts of glass components passing into solution on the additions of Al_2O_3 to the sodium disilicate compound when these glasses are treated with 0.1 and 1N solutions of hydrochloric acid. We see that the increase in concentration of hydrochloric acid over the indicated range shifts the stability maximum into the region of aluminosilicates with a lower Al_2O_3 content. This reflects the absence of correlation between decomposability and the position of the singular points on the investigated portion of the phase diagram of the system $Na_2O-Al_2O_3-SiO_2$.

The curves of Figure 2 illustrate the character of the decomposition of vitreous sodium aluminosilicates. For glasses with addition of up to 0.15 mole Al_2O_3 to the disilicate, the decomposition is mainly characterized by a process of leaching-out of Na_2O. With increasing content of Al_2O_3 there is a fall in the stability of the aluminosilicate skeleton from which the aluminum ions are washed out in the first instance. The Na_2O and Al_2O_3 leaching curves substantially coincide. Passage into solution of SiO_2 from aluminosilicate glasses lags behind that of other components up to a composition with an Al_2O_3 content of 0.5 mole Al_2O_3.

Silicic acid is capable of passing into solution, when the investigated sodium aluminosilicates are treated with acids, either in the ionic form or in a state close to molecular dispersion. Evidence of this, as indicated above, is the presence in the acid extracts of silicic acid which is directly determinable by a colorimetric method. Passage into solution of silicic acid in the form of ions or in a highly dispersed state has also been observed by Kruger [7] who studied the action of acids on natural lucite by the method of electrodialysis.

A comparison of the decomposability of the investigated aluminosilicates in various acids reveals that 0.1 N sulfuric acid acts more intensively than hydrochloric or nitric acid of the same concentration. We may suggest that this is due to the differing degrees of dissociation of the respective salts which are formed in solution by exchange of the sodium and aluminum ions of the glass by hydrogen ions of the solution.

Acids like hydrochloric and nitric possess a higher mean coefficient of activity than sulfuric acid of the same concentration. In the light of what has been suggested above about the influence of the hydrogen ion concentrations, we ought to expect a higher velocity of decomposition of aluminosilicates in solutions of the former acids. As we know, however, in passing from singly charged to multiply charged ions there is a sharp fall in the degree of dissociation of the resultant electrolytes [8]. Consequently the sodium sulfate and, in particular, the aluminum sulfate formed in the solution will be very much less dissociated than the corresponding chlorides and nitrates. And this difference will be greater than the difference in the degree of electrolytic dissociation of hydrochloric and sulfuric acids. The concentration of sodium and aluminum ions in the solution decreases sharply in the case of reaction with sulfuric acid in comparison with reaction with hydrochloric and nitric acids, due to which the removal of sodium and aluminum ions from the glass is accelerated.

Consequently, as follows from the considerations put forward above, a number of factors govern the rate of decomposition of vitreous sodium aluminosilicates in solutions of acids. The most important of these are the hydrogen ion concentration of the reacting solution, the state of the residual aluminosilicate surface film, and the degree of dissociation of the electrolytes which are formed in solution.

SUMMARY

1. A study was made of the reaction with solutions of hydrochloric, nitric and sulfuric acids of vitreous sodium aluminosilicates composed of disilicate with additions of 0.15 to 1 mole Al_2O_3.

2. Increasing hydrogen ion concentration when using one and the same acid is accompanied by increasing decomposability of those aluminosilicate glasses whose skeleton, due to depolymerization of their silica content, is unstable toward solutions of acids.

3. Vitreous sodium aluminosilicates are decomposed in 0.1 N sulfuric acid solution more rapidly than in hydrochloric and nitric acids of the same concentration. This phenomenon can be explained by the lower degree of electrolytic dissociation in comparison with the corresponding chlorides and nitrates formed in a solution of sodium and aluminum sulfates.

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Received November 19, 1953

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* (T.p. = Consultants Bureau Translation pagination).

REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

COMMUNICATION 5. REACTION OF VITREOUS SODIUM ALUMINOSILICATES WITH WATER

Yu. A. Shmidt

In previous communications we described the reaction of vitreous sodium silicates with aqueous solutions [1,2], and also the reaction of vitreous sodium aluminosilicates with solutions of acids [3,4]. The present paper deals with the reaction of vitreous sodium aluminosilicates with water.

The literature on this topic is very scanty. Dimbleby and Turner [5], studied six sodium aluminosilicate glasses which were prepared by successive substitution in a starting glass, composition $Na_2O \cdot 3SiO_2$, of up to 0.3 mole Na_2O by alumina (in 0.05 mole steps). They determined the loss in weight of powders of the glass after boiling in water. In a study by Enss [6] the starting substance was a glass composed of Na_2O 18% and SiO_2 82%, in which part of the silica was replaced by alumina. After heating the powdered glass in water at 100°, the Na_2O, Al_2O_3 and SiO_2 contents of the solution were determined. Our recalculation of Enss' results shows that the leached surface film of the glass is slightly enriched with alumina by comparison with the original glass. Studies [5] and [6] also showed that the chemical stability of the glasses rises appreciably with increasing content of alumina and that a relatively greater effect is exerted by the first, small, additions. In a study of the decomposition of feldspars by aqueous solutions, Correns [7] showed that in acidic and alkaline media the leached film contains less alumina and in a neutral medium it contains more alumina than the original mineral. The author correlates this behavior with the amphoteric character of alumina, which in the neutral region possesses minimum solubility.

EXPERIMENTAL

The reaction with water was studied of twelve vitreous sodium aluminosilicates prepared by adding various amounts of alumina to the previously studied sodium silicates (see Table 1). The position on the phase diagram of the silicates and aluminosilicates investigated in the present research and in the above-noted papers [5,6] are shown in Figure 1. The chemical analysis of the investigated glasses of the sodium disilicate series has been previously reported [3].

TABLE 1

Composition of the sodium aluminosilicates studied

Starting silicate	Aluminosilicates				
Molar ratio of $Na_2O : SiO_2$	Molar ratio of $Na_2O : Al_2O_3 : SiO_2$				
1:1.4	1:0.05:1.4	1:0.15:1.4	1:0.3:1.4	——	——
1:1.7	1:0.05:1.7	1:0.15:1.7	1:0.3:1.7	——	——
1:2	1:0.05:2	1:0.15:2	1:0.3:2	1:0.5:2	1:1:2
1:3	1:0.05:3	——	——	——	——

Experiments were carried out at 40° by the previously described procedure [1,3], i.e., by determination of the quantity of components passing into solution after a specified period of reaction of the sample with water. In the case of the aluminosilicate with the composition $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ the amounts of components passing into solution were so small that we decided to resort to the powder method. We used a glass powder with a particle size of 110-140 μ, thoroughly washed free from dust with ethanol and dried at 110°. The calculated surface area of the weighed sample (0.8 g) used was approx. 160 cm^2. As previously, we characterized the process of reaction on the basis of the magnitudes of n_{Na_2O} $n_{Al_2O_3}$, and n_{SiO_2} (representing the amount of the respective oxides passing from the glass into solution from 1 cm^2 of glass surface), and also with reference to the magnitudes of α and β (representing the proportions of Al_2O_3 and SiO_2 passing into solution from the surface film of the glass brought into reaction with the solution).

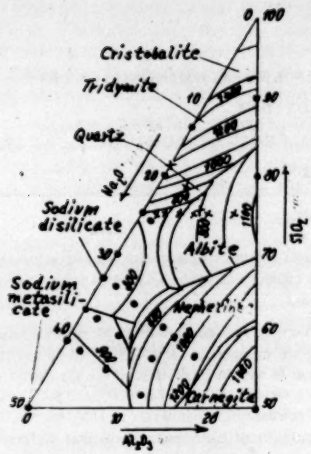

Fig. 1. Position of the investigated compositions on the $Na_2O-Al_2O_3-SiO_2$ phase diagram: - compositions studied in the present investigation; X - studied by Dimbleby and Turner; + - studied by Enss.

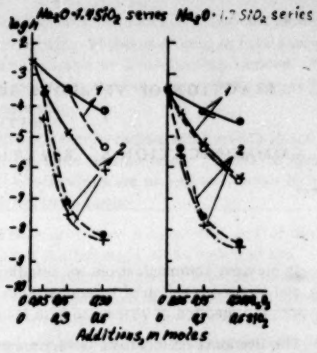

Fig. 2. Comparison of amounts of components passing into solution after 6 hours' reaction with water of vitreous sodium silicates and aluminosilicates (1 - silicates; 2 - aluminosilicates): $-\cdot-\cdot-$ $\log n_{Na_2O}$ $-\cdot-\cdot-$ $\log \frac{n_{Al_2O_3}}{k}$; $-\cdot-\cdot-$ $\log \frac{n_{SiO_2}}{m}$

(k and m are the Al_2O_3 and SiO_2 contents of the glass expressed in the form $Na_2O \cdot kAl_2O_3 \cdot mSiO_2$.)

In view of the fact that the regularities observed in the investigated series of aluminosilicates were analogous, we shall in the future concentrate for the most part on the sodium disilicate series which we studied up to addition of one mole alumina. Results of investigation of reaction with water of some glasses of this series over various intervals are set forth in Table 2. In Figures 2 and 3 are compared the amounts of components passing into solution after six hours' reaction with water of the vitreous sodium silicates and aluminosilicates investigated by us. On the basis of these data and of literature data [8,9] we suggest that aluminum enters into the structure of the studied glasses in fourfold coordination as an analog of silicon, and that consequently 0.5 mole alumina is approximately equivalent to one mole of silica in the structure of the glass.

From the data obtained we see that addition of alumina to sodium disilicate is accompanied by a continuous drop in the amounts of Na_2O passing into solution, this drop being relatively more pronounced with small additions. Up to additions of 0.15 mole Al_2O_3 the values of $n_{Al_2O_3}$ and n_{SiO_2} are reduced very much more quickly than the magnitude of n_{Na_2O}. With further increase of the additions of alumina (0.3 and 0.5 mole) the fall in values of $n_{Al_2O_3}$ and n_{SiO_2} becomes less marked, and later it ceases entirely. On transition to the composition $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ these values rise appreciably. A consequence of the described change of $n_{Al_2O_3}$ and n_{SiO_2} is that the magnitudes of α and β, which at first (up to addition of 0.15 mole Al_2O_3) fell off, subsequently started to rise again and for the composition $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ they reached fairly high values ($\alpha = 0.42$, $\beta = 0.17$).

Comparison of the data obtained for aluminosilicates with an identical (in moles) addition of alumina shows that with increase of their silica content the amount of components passing into solution continuously decreases, in analogy with what took place in the sodium disilicate series. It should also be noted that the magnitude of β in all cases is lower than that of α, thus pointing to enrichment of the surface film with alumina.

Evaluation of results

As we have already reported [3,4], with increasing addition of alumina to sodium silicates there is an increase in the total number of Si-O-Al bonds. In other words the degree of polymerization of the aluminosilicate skeleton of the glass increases. The number of Si-O-Si bonds, however, i.e., the degree of polymerization of the silica portion of the skeleton, decreases during the process. For this reason, the influence of alumina on the reaction of glasses with aqueous solutions has a dual character.

TABLE 2

Reaction of some aluminosilicates of the disilicate series with water

Composition of glass	Characteristics	Duration in hours				
		1	2	4	6	8
$Na_2O \cdot 2SiO_2$	$n_{Na_2O} \cdot 10^{-6}$	18	30	47	62	76
	$n_{SiO_2} \cdot 10^{-6}$	3,2	4,2	5,8	9,3	13
$Na_2O \cdot 0,05Al_2O_3 \cdot 2SiO_2$	$n_{Na_2O} \cdot 10^{-6}$	8,0	11	17	22	25
	$n_{Al_2O_3} \cdot 10^{-6}$	0,003	0,005	0,012	0,020	0,024
	$n_{SiO_2} \cdot 10^{-6}$	0,022	0,34	0,64	1,2	1,4
	α	0,014	0,015	0,019	0,027	0,028
	β	0,008	0,009	0,014	0,018	0,019
$Na_2O \cdot 0,15Al_2O_3 \cdot 2SiO_2$	$n_{Na_2O} \cdot 10^{-6}$	1,5	2,0	2,7	3,3	3,8
	$n_{Al_2O_3} \cdot 10^{-6}$	—	—	—	0,001	—
	$n_{SiO_2} \cdot 10^{-6}$	—	—	—	0,022	—
	α	—	—	—	0,003	—
	β	—	—	—	0,002	—
$Na_2O \cdot 0,3Al_2O_3 \cdot 2SiO_2$	$n_{Na_2O} \cdot 10^{-6}$	0,18	0,22	0,26	0,31	0,34
	$n_{Al_2O_3} \cdot 10^{-6}$	—	—	—	0,0004	—
	$n_{SiO_2} \cdot 10^{-6}$	—	—	—	0,004	—
	α	—	—	—	0,006	—
	β	—	—	—	0,004	—

On the one hand an increase in the degree of polymerization of the aluminosilicate framework of the glass strengthens all the bonds, as was the case when the silica content of vitreous sodium silicates was increased [1]. Consequently the amounts of Na_2O passing into solution (likewise the amounts of Al_2O_3 and SiO_2 when the amounts of alumina added are small) decrease sharply. The influence of the alumina is then very much greater than that of the equivalent amounts of silica. Attention must also be directed to the fact that the addition to sodium disilicate of only 0,05 mole Al_2O_3 lowers the value of n_{Na_2O} 2,8 times and that of n_{SiO_2} 7,8 times (the values are compared after 6 hours' reaction). Further increase of the content of alumina to 0,15 mole lowers these values (by comparison with disilicate) 19 and 420 times respectively. At the same time it is easy to calculate that in the case of addition of 0,05 mole Al_2O_3 only 5% of the total number of sodium ions and 10% of the SiO_4 tetrahedra are directly bound to the AlO_4 tetrahedra, while in the case of addition of 0,15 mole Al_2O_3 the amounts are respectively 15 and 60%. These data indicate that the influence of the aluminum extends not only to those sodium ions and SiO_4 tetrahedra which are directly linked to the AlO_4 tetrahedra but also to the whole structure of the glass. Slight depolymerization of the silicate portion of the framework with small additions of alumina does not occur to an appreciable extent since the AlO_4 tetrahedra are surrounded by a large number of SiO_4 tetrahedra and are thereby protected against the action of the solution.

When the alumina content in the sodium disilicate series is increased to 0,3 mole and higher, the number of Si–O– Al bonds is then higher than the number of Si–O–Si bonds, the AlO_4 tetrahedra becoming more accessible to the action of the solution. Hence, as was shown in previous communications [3,4], depolymerization of the silicate portion of the framework beyond the above-indicated limit has the consequence that under the action of solutions of acids which extract aluminum ions from the residual film, this film at first becomes loose and then completely decomposes.

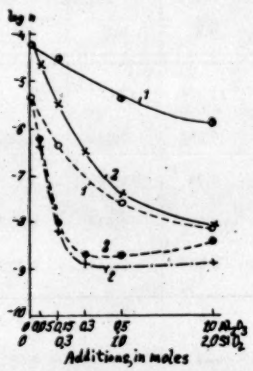

Fig. 3. Comparison of amounts of components passing into solution after 6 hours' reaction with water of vitreous sodium silicates and aluminosilicates (sodium disilicate series: 1 - silicates; 2 - aluminosilicates): —— $\log n_{Na_2O}$; - - - $\log \frac{n_{Al_2O_3}}{k}$; – – – $\log \frac{n_{SiO_2}}{m}$

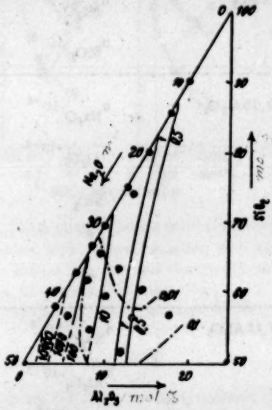

Fig. 4. Amount of Na_2O (in moles / $cm^2 \cdot 10^{-6}$) passing into solution and magnitude of a as functions of the composition of the studied glasses: ——— n_{Na_2O}; — — — a

When the glasses react with water, the passage of aluminum ions into solution is inhibited by the near insolubility of alumina in neutral and weakly alkaline solutions, due to which there is no intensive decomposition of the film. Increase, however, of the content of alumina in the sodium disilicate series to more than 0,3-0,5 mole leads nevertheless to a slight increase in the amounts of Al_2O_3 and SiO_2 passing into solution. Increase in the silica content of the composition of the vitreous sodium aluminosilicates is accompanied by an increased degree of polymerization both of the aluminosilicate framework as a whole and of the silicate portion, due to which the quantity of components passing into solution continuously diminishes.

As was pointed out above, the alumina content of the residual film is observed in all the experiments to be higher than that of the original glass. It may therefore be suggested that during the primary process of exchange of the sodium ions of the glass by hydrogen ions from the solution which leads to formation of a film, the bonds between the AlO_4 and SiO_4 tetrahedra entering into the aluminosilicate framework are not broken. Enrichment of the film itself with alumina evidently occurs as the result of reverse adsorption of those aluminum ions which had gone into solution from the portion of the film which had been completely decomposed in the course of the experiment. If we know the composition of the resultant solution, we can make a rough calculation of both the total content of aluminum in the film and of the content of aluminum entering into the aluminosilicate framework of the film and, separately, adsorbed by it. Calculations show that with increasing stability of the aluminosilicates, both the absolute and relative content of aluminum adsorbed in the film falls sharply and amounts to not more than 0,2-0,5 % of its total content. This enables us to conclude that the main influence upon the stability of the residual film is evidently exerted by the aluminum ions entering into the structure of its aluminosilicate framework. The small amount of adsorbed aluminum ions, however, which are retained in the film by relatively weak adsorption forces can hardly exert an appreciable influence on its stability. This view is also strengthened by experiments in an acid medium [3,4] with small additions of alumina which brought about strengthening of the film. In spite of the fact that in an acid medium the aluminum content of the film is reduced,

due to which its reverse adsorption is obviously insignificant, the values of n_{Na_2O} prove to be close to those obtained in experiments with water. The small difference in values of n_{Na_2O} which nevertheless arise may be accounted for by the high hydrogen ion concentration in the acidic medium [2] and not by difference in the stability of the film.

In Figure 4 lines have been plotted by interpolation which correspond to equal amounts of Na_2O passing into solution in the investigated region of compositions. On the same diagram (dot-dash curves) are shown plots corresponding to the values of $\alpha = 0{,}1$ and $0{,}01$. A comparison of Figures 1 and 4 does not reveal any correspondence whatever between the amount of components passing into solution and the phase diagram of the system $Na_2O-Al_2O_3-SiO_2$.

SUMMARY

1. Increase in the alumina content of sodium aluminosilicates is accompanied by an increased degree of polymerization of the aluminosilicate framework of the glass, leading to a considerable drop in the amounts of Na_2O passing into solution as well as (in the case of small additions of alumina) of the amounts of Al_2O_3 and SiO_2 passing into solution. In this connection the influence of alumina is much stronger than that of equivalent amounts of silica.

2. When the alumina content increases beyond a certain limit, the depolymerization of the silicate portion of the framework weakens the stability of the residual film at the surface of vitreous sodium aluminosilicates.

3. An increase of the silica content continuously reduces the amounts of components passing into solution.

4. A large proportion of the aluminum ions in the residual film enters into the composition of its aluminosilicate framework and therefore has an essential influence on its strength. A small proportion of the aluminum ions is evidently retained by the film in the adsorbed state.

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Received November 19, 1953

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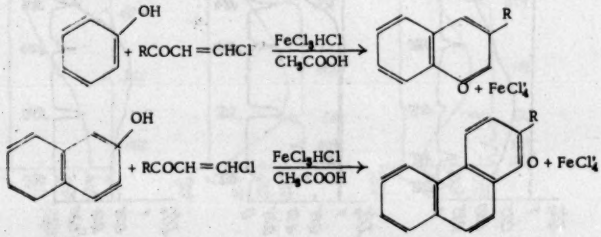
ABSORPTION SPECTRA OF PYRILIUM SALTS

A. N. Nesmeyanov, L. A. Kazitsyna, N. K. Kochetkov and M. N. Rybinskaya

Three of us have realized a new synthesis of benzopyrilium [1], flavylium [1] and naphthopyrilium [1,2] salts. These compounds, prepared according to the scheme



in the form of oxonium salts containing the $FeCl_4$ anion, form intensely colored crystalline powders, soluble in glacial acetic acid. One of them, 7-hydroxy-4-methoxyflavylium chloride, contains a cation which is the methyl derivative of the anthocyanidine, hesperidine, found in Geneseneria cardinalis.

The literature contains rather scanty data for the absorption spectra of pyrilium salts. Wizinger plotted the absorption spectra of various distyrylpyrilium salts [3] and of some flavylium salts [4], but he only gave the wavelengths of the absorption maxima. We took advantage of the great possibilities of the new spectrophotometer constructed by Dianov-Klokov in the laboratory of I. V. Obreimov (Institute of Organic Chemistry of the Academy of Sciences USSR) to plot the absorption spectra of the following pyrilium salts: benzopyrilium – 2-methylbenzopyrilium ferrichloride (I), 2,6-dimethylbenzopyrilium ferrichloride (II), 6-hydroxy-2-methylbenzopyrilium ferrichloride (III), and 7-hydroxy-2-methylbenzopyrilium ferrichloride (IV); flavylium – flavylium ferrichloride (V), 2-methylflavylium ferrichloride (VI), 4',6-dimethylflavylium ferrichloride (VII), 4'-bromo-6-methylflavylium ferrichloride (VIII), 6-hydroxyflavylium ferrichloride (IX), 4'-bromo-6-hydroxyflavylium ferrichloride (X), 4'-bromo-7-hydroxyflavylium ferrichloride (XII), 7-hydroxy-4'-methoxyflavylium ferrichloride (XIII); naphthopyrilium salts – 2-methylnaphthopyrilium ferrichloride (XIV), 2-propylnaphthopyrilium ferrichloride (XV), 2-isopropylnaphthopyrilium ferrichloride (XVI), 2-isobutylnaphthopyrilium ferrichloride (XVII), 2-amylnaphthopyrilium ferrichloride (XVIII), 2-phenylnaphthopyrilium ferrichloride (XIX), 2-p-tolylnaphthopyrilium ferrichloride (XX), 2-p-bromophenylnaphthopyrilium ferrichloride (XXI), 2-p-methoxyphenylnaphthopyrilium ferrichloride (XXII), and 2-methylnaphthopyrilium perchlorate (XXIII).

Spectra of pyrilium salts in acetic acid were plotted in the 587 to 334 mμ region at 10^{-4} concentration of solutions; the curves of the absorption spectra (ratio of I/I_0) obtained on the oscillograph were directly photographed onto a plate. At a later date we intend to plot the absorption curves of the enumerated compounds in the ultraviolet region.

In order to establish the effect of the contribution of the anion in the plotted spectrum, we plotted the spectrum of ferric chloride in a solution of acetic and hydrochloric acids. It was found that appreciable absorption of the $FeCl'_4$ anion commences at a concentration of 10^{-2} and its absorption can clearly not bring about a serious change in the spectra of the salts, since we carried out the examination of the absorption spectra of the pyrilium salts at a concentration of 10^{-4}. In order to determine the influence of various anions upon the character of the absorption, we plotted the absorption spectra of 2-methylnaphthopyrilium ferrichloride and perchlorate. We see from the photographs (XXIII and XIV) that the spectrum of the salt does not substantially alter with change of anion. We may therefore assume that the absorption spectra of the investigated compounds are governed by the organic portion of the molecule.

The spectra of the investigated pyrilium salts differ profoundly in dependence on the structure; in respect of the character of the absorption spectra all the investigated substances may be arranged into three groups: benzopyrilium, flavylium, and naphthopyrilium salts.

EXPERIMENTAL

Benzopyrilium Salts

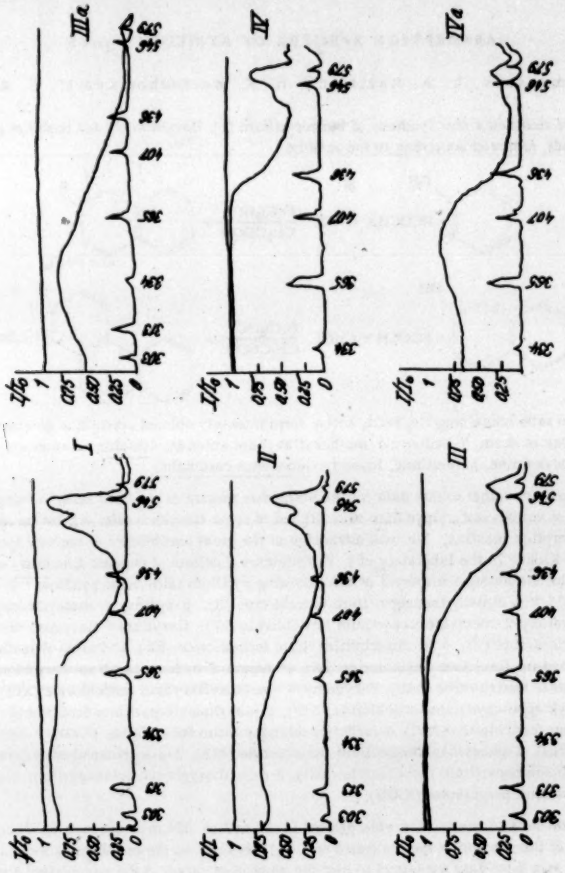


Figure 1.

The properties of the benzopyrilium salts are set forth in Table 1.

The spectrum of benzopyrilium salts in the 579-334 mμ region exhibits a characteristic absorption band in the 570-500 m μ region with an oscillatory structure; this band can clearly serve for identification of benzopyrilium salts. Replacement of the hydrogens in the 6 and 7 position by alkyl and hydroxyl groups shifts the band without changing its character; in this connection we may note that the CH_3 group in the 6-position very slightly shifts the band in the direction of longer waves and that a bigger shift occurs with compounds containing hydroxyl groups in the 6- and 7- positions, although to our surprise no change occurred in the character of the band either on introduction of the OH group or of change in its position. The character of the resultant absorption of benzopyrilium salts is insignificantly affected by the substituents and their position; for I, II and III there are two overlapping bands which are shifted in the direction of longer waves when the hydrogen in position 6 is replaced by methyl and hydroxyl groups; hence for the three bands of compounds I, II and III we observe the same characteristic as for the first band. Introduction of the OH group into the 7- position completely changes the character of the absorption in the 436-334 m μ region, which is fully consistent with our investigations of the absorption spectra of flavylium salts.

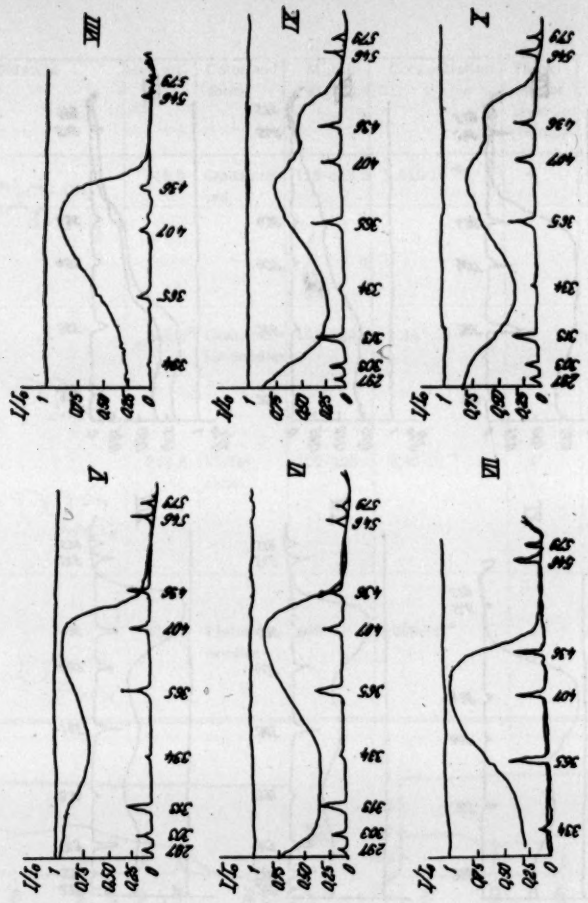


Fig. 2.

Flavylium salts

The properties of flavylium salts are set forth in Table 2.

The absorption spectra of the investigated flavylium salts essentially depend upon the character and position of the substituents. Methyl groups in the 6- and 4'-positions and bromine in the 4'-position do not alter the form of the spectrum and only shift it to an insignificant extent in the direction of long waves; a greater effect on the shift is exerted by a substituent in the 4'-position. The form of the absorption curve is completely altered by introducing a hydroxyl group into the molecule, and the position of the hydroxyl group has a significant influence upon the character of the spectrum: Pyrilium salts with a hydroxyl group in the 6-position exhibit two absorption bands and the intensity of absorption of the second is greater than that of the first; substitution of the hydrogen in the 4'-position of 6-hydroxyflavylium ferrichloride leads to the usual shift of the spectrum in the long-wave direction without change of character; the absorption spectrum of 7-hydroxyflavylium ferrichloride also contains two absorption bands, but the intensity of the first is considerably greater than that of the second; substitution of the hydrogen in the 4'-position by bromine and methoxyl leads to the usual shift toward the red without change in the character of the spectrum.

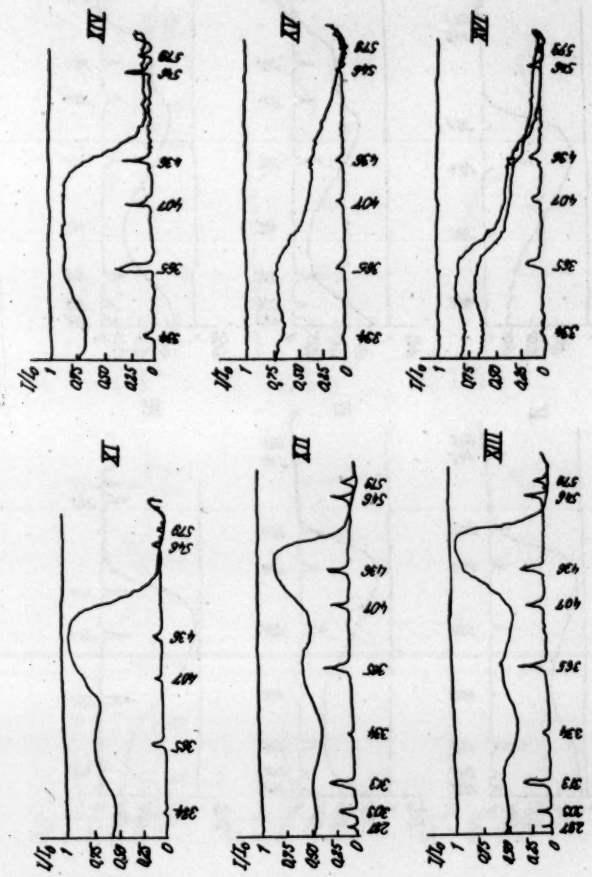


Fig. 3.

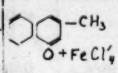
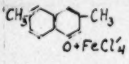
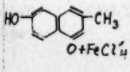
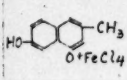
Naphthopyrilium salts

The properties of the naphthopyrilium salts are set forth in Table 3.

We plotted the absorption spectra of naphthopyrilium salts containing alkyl and aryl groups in the 2-position. The character of the absorption depends to a marked extent on the substituent; salts containing alkyl radicals (apart from methyl) have similar spectra whose maxima are shifted more and more toward the red with increasing size of radical (we only measured the maximum of the second conspicuous band); salts with phenyl radicals in the 2-position exhibit in the visible region one conspicuous absorption band whose maximum depends upon the substituent in the phenyl radical and which is shifted toward the red when the hydrogen in the para position is replaced by methyl, bromine, and methoxyl.

The investigated absorption spectra of pyrilium salts depend so characteristically on the structure that they can obviously serve for identification of the respective compounds, and in individual cases also for determination of the position of the substituent (hydroxyflavylium compounds.

TABLE 1

Substance	Formula	Mol. wt.	Color and form	M.p. in deg. C.	Concentration	Thickness of layer (in mm)	λ_{max} B mμ	εmax	Absorption spectrum
1. 2-Methylbenzopyrilium ferrichloride		342.8	Cranberry red	125-125.3	$2.419 \cdot 10^{-4}$	4	545 500 324	$8.78 \cdot 10^2$ $5.94 \cdot 10^2$ $9.09 \cdot 10^2$	 I
2. 2,6-Dimethylbenzopyrilium ferrichloride		356.8	Dark-violet needles	103-105	$1.157 \cdot 10^{-4}$	4	548 508 332	$6.37 \cdot 10^2$ $4.14 \cdot 10^2$ $9.55 \cdot 10^2$	 II
3. 6-Hydroxy-2-methylbenzopyrilium ferrichloride		358.8	Violet cubes	122-123	$9.42 \cdot 10^{-4}$	4 1	560 516 337	$0.611 \cdot 10^2$ $0.452 \cdot 10^2$ $7.76 \cdot 10^2$	 III IIIa
4. 7-Hydroxy-2-methylbenzopyrilium ferrichloride		410.9	Violet needles	145	$3.682 \cdot 10^{-4}$	4 1	570 526 386	$4.27 \cdot 10^2$ $2.38 \cdot 10^2$ $2.17 \cdot 10^2$	 IV IVa

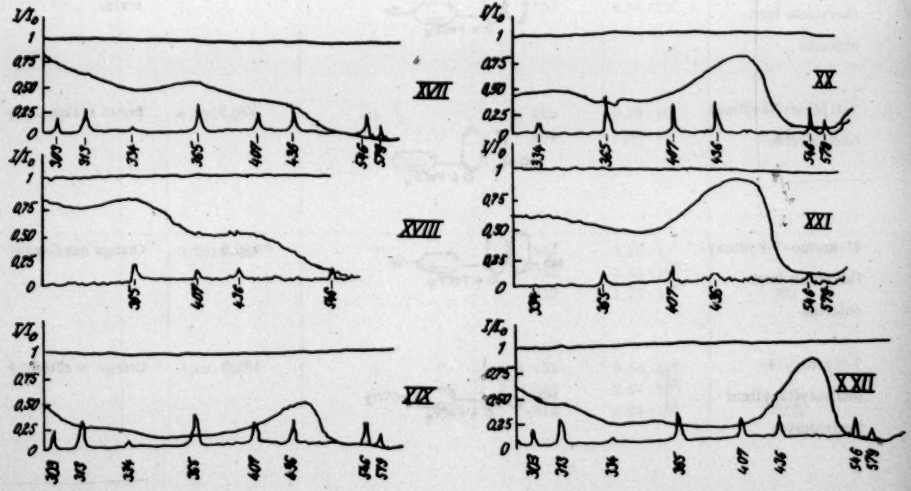
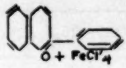
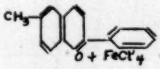
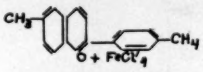
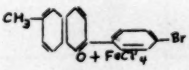
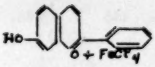
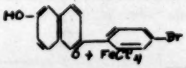
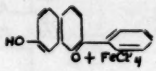
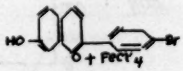
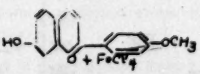


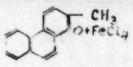
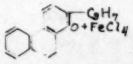
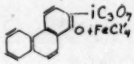
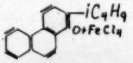
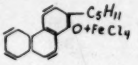
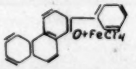
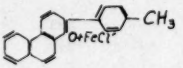
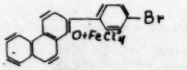
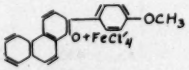
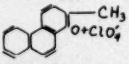
Fig. 4

TABLE 1

Substance	Formula	Mol. wt.	Color and form
Flavylium ferrichloride		404.9	Golden-yellow scales
6-Methylflavylium ferrichloride		418.9	Golden-yellow needles
4',6-Dimethylflavylium ferrichloride		439.9	Yellow needles
4'-Bromo-6-methyl-flavylium ferri-chloride		497.8	Yellow needles
6-Hydroxyflavylium ferrichloride		420.9	Brown scales
4-Bromo-6-hydroxy-flavylium ferri-chloride		499.8	Brick-brown scales
7-Hydroxyflavylium ferrichloride		420.9	Brown scales
4'-Bromo-7-hydroxy-flavylium ferri-chloride		499.9	Orange needles
7-Hydroxy-4'-methoxyflavylium ferrichloride		451.9	Orange needles

M.p. in deg C	Concentration	Thickness of layer (in mm)	λ_{max} in mμ	ϵ_{max}	Absorption spectrum
137-138	$0.972 \cdot 10^{-4}$	4	393	$3.43 \cdot 10^3$	V
170-171.5	$1.856 \cdot 10^{-4}$	4	400	$1.39 \cdot 10^3$	VI
199-200	$0.9374 \cdot 10^{-4}$	4	412	$2.56 \cdot 10^3$	VII
183	$1.695 \cdot 10^{-4}$	2	410	$3.68 \cdot 10^3$	VIII
158-159	$0.687 \cdot 10^{-4}$	4	434 357	$1.13 \cdot 10^3$ $2.11 \cdot 10^3$	IX
190-191.5	$1.038 \cdot 10^{-4}$	2	440 393	$1.87 \cdot 10^3$ $3.04 \cdot 10^3$	X
158-159	$4.088 \cdot 10^{-4}$	1	433 365	$3.26 \cdot 10^3$ $1.42 \cdot 10^3$	XI
169	$0.2519 \cdot 10^{-4}$	1	444 366 312	$3.25 \cdot 10^4$ $1.51 \cdot 10^4$ $1.27 \cdot 10^4$	XII
176-177	$4.23 \cdot 10^{-4}$	1	452 365 316	$3.86 \cdot 10^3$ $8.04 \cdot 10^3$ $8.04 \cdot 10^3$	XIII

TABLE 3

Compound	Formula	Mol. wt.	Color and form
2-Methylnaphthopyrilium ferrichloride		392.9	Dark-green needles
2-Propylnaphthopyrilium ferrichloride		420.9	Light-green scales
2-Isopropylnaphtho-pyrilium ferrichloride		420.9	Yellow needles
2-Isobutylnaphtho-pyrilium ferrichloride		434.9	Yellow scales
2-Amylnaphtho-pyrilium ferri-chloride		449.0	Red-brown scales
2-Phenylnaphtho-pyrilium ferri-chloride		454.9	Orange needles
4'-Methyl-2-phenyl-naphthopyrilium ferrichloride		468.9	Light-orange needles
4'-Bromo-2-phenyl-naphthopyrilium ferrichloride		533.88	Orange needles
4'-Methoxy-2-phenylnaphthopyrilium ferrichloride		484.9	Red needles
2-Methylnaphtho-pyrilium perchlorate		294.7	Dark-green crystals

M.p. in °C	Concentration	Thickness of layer (in mm)	λ_{max} in mμ	ϵ_{max}	Absorption spectrum
152	$2{,}36 \cdot 10^{-4}$	4	366-407	$6{,}15 \cdot 10^{2}$	XIV
124	$0{,}309 \cdot 10^{-4}$	2	358	$8{,}58 \cdot 10^{3}$	XV
100,5 again at 157	$4{,}12 \cdot 10^{-4}$	2	350	$9{,}95 \cdot 10^{2}$	XVI
183	$1{,}39 \cdot 10^{-4}$	4	363	$6{,}47 \cdot 10^{2}$	XVII
74	$1{,}72 \cdot 10^{-4}$	4	365	$1{,}06 \cdot 10^{3}$	XVIII
187,5-188	$0{,}268 \cdot 10^{-4}$	4	448	$2{,}80 \cdot 10^{3}$	XIX
166-168	$0{,}737 \cdot 10^{-4}$	4	457	$0{,}37 \cdot 10^{2}$	XX
216-217	$1{,}11 \cdot 10^{-4}$	4	458	$1{,}55 \cdot 10^{3}$	XXI
206-207	$0{,}387 \cdot 10^{-4}$	4	474	$4{,}97 \cdot 10^{2}$	XXII
180	$1{,}59 \cdot 10^{-5}$	1	407	$8{,}43 \cdot 10^{3}$	XXIII

Fig. 5

We express our gratitude to I. V. Obreimov for guidance in the research and to I. A. Palitsyna for assistance in plotting the absorption spectra.

SUMMARY

1. Absorption spectra were plotted of four benzopyrilium, nine flavylium and ten naphthopyrilium salts in the 579-334 mμ region.

2. It was established that the absorption spectrum in the visible region can serve for identification of the structure of a pyrilium salt and in some cases can give information about the position of a substituent.

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Received December 8, 1953

Moscow M. V. Lomonosov State University

* (T.p. = Consultants Bureau Translation Pagination)

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 2. β-ALKOXY (PHENOXY) VINYLTHIOPHOSPHONYL AND β-ARYLVINYLTHIOPHOSPHONYL CHLORIDES

K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov

The alkylthiophosphonyl chlorides have been little investigated. Regarding the chlorides of thiophosphonic acids containing unsaturated radicals, not a single reference to them could be found in the literature. We have developed a perfectly accessible and convenient method of preparation of β-alkoxy(phenoxy)-vinylthiophosphonyl and β-arylvinylthiophosphonyl chlorides. The method starts from crystalline products of addition of phosphorus pentachloride to vinyl ethers($ROCHCl-CH_2PCl_4 \cdot PCl_5$), described in previous communications [1]. These are treated with hydrogen sulfide until the solid substance has been completely transformed into a liquid. The reaction proceeds in one direction with slight evolution of heat without formation of any secondary products and gives yields of over 90%. Reaction scheme:

$$ROCHCl \cdot CH_2PCl_4 \cdot PCl_5 + H_2S = ROCH{=}CHPSCl_2 + PSCl_3 + 3HCl.$$

By this method we prepared for the first time the following acid chlorides: β-ethoxyvinylthiophosphonyl chloride; β-isopropoxyvinylthiophosphonyl chloride; β-butoxyvinylthiophosphonyl chloride; β-n-hexoxyvinylthiophosphonyl chloride; β-phenoxyvinylthiophosphonyl chloride; and β-phenylvinylthiophosphonyl chloride. Their physical properties are set forth in the table. The chlorides of β-alkoxy(phenoxy)-vinylthiophosphonic and of β-arylvinylthiophosphonic acids are transparent liquids, readily soluble in common organic solvents, insoluble in water, and stable to hydrolysis. The chlorides of thiophosphonic acids which we prepared differ from the chlorides of β-alkoxy(phenoxy)-vinylthiophosphonic and β-arylvinylphosphonic acids in hardly entering into reaction with alcohols.

Formula	B.p. in °C (p in mm mercury)	n_D^{20}	d_4^{20}	Yield in %
$C_2H_5OCH = CHPSCl_2$	84 (2)	1.5422	1.3334	74
$i\text{-}C_3H_7OCH = CHPSCl_2$	92 (2)	1.5224	1.2684	75
$n\text{-}C_4H_9OCH = CHPSCl_2$	105 (2)	1.5234	1.2471	77
$n\text{-}C_6H_{13}OCH = CHPSCl_2$	128 (2)	1.5255	1.1841	60
$C_6H_6OCH = CHPSCl_2$	130 (1)	1.6086	1.1670	80
$C_6H_5CH = CHPSCl_2$	130 (2)	1.6439	1.3533	91

The boiling points of the β-alkoxy(phenoxy)-vinylphosphonyl chlorides are approximately the same as those of the β-alkoxy(phenoxy)-vinylthiophosphonyl chlorides, but the refractive indices and specific gravities of the β-alkoxy(phenoxy)-vinylthiophosphonyl chlorides are considerably higher than those of the oxygenated derivatives. There is also a difference in the reactivities of the acid chlorides. The β-alkoxy(phenoxy)-vinylphosphonyl chlorides are more reactive in chlorine exchange reaction than are the β-alkoxy(phenoxy)-vinylthiophosphonyl chlorides.

EXPERIMENTAL

β-Ethoxyvinylthiophosphonyl chloride $C_2H_5OCH = CHPSCl_2$. Into a three-necked flask fitted with mechanical stirrer, reflux condenser and dropping funnel were charged 300 ml dry benzene and 83 g PCl_5. Dropwise addition was made to the resultant suspension of 14.2 g vinylethyl ether dissolved in 15 ml benzene. Crystals separated during the addition of the ether, and after the whole amount of ether had been added a copious

crystalline precipitate had formed. The next day the latter was heated on a water bath with stirring at 60-65° for 30 min. After cooling, dry hydrogen sulfide was passed through. Hydrogen chloride was evolved during this process and heat was released by the reaction mass. The addition product was gradually converted into the thiophosphonyl chloride. Gas was passed through until the precipitate had completely dissolved and the liquid had cooled. After distilling off the benzene and phosphorus thiochloride, the residue was kept on a boiling water bath in the vacuum of a water pump for about an hour and then fractionated at 2 mm to give 30 g substance (74% of the theoretical); b.p. 84° (2 mm): n_D^{20} 1.5422 d_4^{20} 1.3334.

Found %: C 23.76; 23.73; H 3.65; 3.75; P 14.99; 15.12
$C_4H_7OPSCl_2$. Calculated %: C 23.41; H 3.41; P 15.11

β-Ethoxyvinylthiophosphonyl chloride is a pale-yellow liquid, stable to hydrolysis by water; it is non-reactive at room temperature with alcohols; soluble in common organic solvents.

β-Isopropoxyvinylthiophosphonyl chloride i-$C_3H_7OCH{=}{=}CHPSCl_2$. To a suspension of 83 g PCl_5 in 250 ml dry benzene was gradually added, with energetic stirring, 12.2 g vinylisopropyl ether in 15 ml benzene; the reaction mass was then worked up as above. Yield 33 g (75% of the theoretical); b.p. 92° (2 mm); n_D^{20} 1.5224; d_4^{20} 1.2864.

Found %: C 27.52; 27.60; H 3.96; 3.82; P 14.02; 14.04
$C_5H_9OPSCl_2$. Calculated %: C 27.39; H 4.10; P 14.15

β-Isopropoxyvinylthiophosphonyl chloride is an easily distillable liquid with the characteristic odor of an acid chloride; its properties resemble those of the preceding substance.

β-n-Butoxyvinylthiophosphonyl chloride n-$C_4H_9OCH = CHPSCl_2$. 20 g vinylbutyl ether, dissolved in an equal volume of benzene, was run with stirring into a suspension of 83 g PCl_5 in 300 ml dry benzene. After passing in hydrogen sulfide and driving off the solvent and the phosphorus thiochloride, β-n-butoxyvinylthiophosphonyl chloride was isolated in a yield of 36 g (77% of the theoretical); b.p. 105° (2 mm); n_D^{20} 1.5234; d_4^{20} 1.2471.

Found %: Cl 30.55; 30.61; P 13.25; 13.29; C 31.36; 31.45; H 4.87; 4.94
$C_6H_{11}OPSCl_2$. Calculated %: Cl 30.47; P 13.30; C 30.90; H 4.72

This acid chloride is a readily mobile liquid with the properties usual for substances of this class.

β-n-Hexoxyvinylthiophosphonyl chloride n-$C_6H_{13}OCH = CHPSCl_2$. 47 g finely pulverized PCl_5 and 150 ml benzene were placed in a flask. Addition was made with stirring of 12.8 g vinylhexyl ether dissolved in an equal volume of benzene. After treatment with hydrogen sulfide and removal of the benzene and phosphorus thiochloride, there was isolated 13.6 g (60% of the theoretical) of the acid chloride. β-n-Hexoxyvinylthiophosphonyl chloride has b.p. 128° (2 mm); n_D^{20} 1.5255; d_4^{20} 1.1841; usual properties.

Found %: C 38.12; 37.80; H 3.00; 2.87½ P 37.94; 12.05; 12.07; H 2.76;
$C_8H_7OPSCl_2$. Calculated %: C 37.94; H 2.76; P 12.25.

β-Phenoxyvinylthiophosphonyl chloride $C_6H_5OCH{=}CHPSCl_2$. Into a suspension of PCl_5 prepared from 83 g PCl_5 and 250 ml benzene was slowly run 24 g vinylphenyl ether. Hydrogen sulfide was passed through the resultant crystalline product, after which the reaction product was worked up in the usual way. Yield 40 g acid chloride; b.p. 140° (1 mm); n_D^{20} 1.6086; d_4^{20} 1.1670.

Found %: C 38.12; 37.80; H 3.00; 2.87; P 37.94; 12.05; 12.07; H 2.76;
$C_8H_7OPSCl_2$. Calculated %: C 37.94; H 2.76; P 12.25. Usual properties.

β-Phenylvinylthiophosphonyl chloride $C_6H_5CH = CHPSCl_2$. 20.8 g freshly distilled dry styrene dissolved in 20 ml benzene was added in several portions to 83 g finely pulverized PCl_5 in 250 ml benzene. After the whole of the styrene had been added, the reaction mass was thoroughly stirred and left overnight. The next day the mass was heated on a water bath at 65-70° for 30 minutes before passing a stream of dry hydrogen sulfide until the precipitate had completely dissolved and the resultant liquid had cooled. After driving off the benzene and the phosphorus thiochloride, the residue was kept in the vacuum of a water jet pump on a boiling water bath for an hour. Yield 43.5 g substance (91% of the theoretical); b.p. 130° (2 mm); n_D^{20} 1.6439; d_4^{20} 1.3533.

Found %: C 40.30; 40.12; H 3.28; 3.22; P 13.08; 13.02
$C_8H_7PSCl_2$. Calculated %: C 40.50; H 2.95; P 13.12

The properties were the same as those of the other β-alkoxyvinylthiophosphonyl chlorides which have been described.

SUMMARY

1. A simple and convenient method was developed for the synthesis of chlorides of β-alkoxy(phenoxy)-vinylthiophosphonic and β-arylvinylthiophosphonic acids by reaction of the products of addition of PCl_5 to vinyl ethers with hydrogen sulfide.

2. The following acid chlorides were prepared and characterized: β-ethoxyvinylthiophosphonyl chloride; β-isopropoxyvinylthiophosphonyl chloride; β-n-butoxyvinylthiophosphonyl chloride; β-n-hexoxyvinylthiophosphonyl chloride; β-phenoxyvinylthiophosphonyl chloride; and β-phenylvinylthiophosphonyl chloride.

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Received November 21, 1953

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* (T.p. = Consultants Bureau Translation Pagination)

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DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 3. β-ALKOXYETHOXYVINYLPHOSPHONYL AND β-ALKOXYETHOXYVINYLTHIOPHOSPHONYL CHLORIDES

K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov

In our preceding communications [1] methods were described for the synthesis of β-alkoxyvinylphosphonyl and β-alkoxyvinylthiophosphonyl chlorides by addition of PCl_5 to vinyl ethers. In the present research we investigated the reaction of PCl_5 with monoalkylvinyl ethers of ethylene glycol (the methylvinyl, ethyl vinyl and n-butylvinyl ethers).

Considerable heat was developed and much hydrogen chloride was evolved on reacting the monoalkylvinyl ethers of ethylene glycol with PCl_5 in benzene. At the end of the reaction a yellowish oily layer was formed which after cooling changed into a dense crystalline mass – the product of addition of two molecules of PCl_5 to a molecule of monoalkylvinyl ether of ethylene glycol.

The following addition products were prepared in the above conditions:

$CH_3-O-CH_2-CH_2-O-CHCl-CH_2\cdot PCl_4\cdot PCl_5$. (1)

$C_2H_5-O-CH_2-CH_2-O-CHCl-CH_2\cdot PCl_4\cdot PCl_5$ (2)

$n\text{-}C_4H_9-O-CH_2-CH_2-O-CHCl-CH_2\cdot PCl_4\cdot PCl_5$. (3)

These were not isolated due to their ease of hydrolysis, and also due to the release of hydrogen chloride both while the reaction was being carried out and on standing.

Without separation from the reaction mixture, these substances were subjected to the action of sulfur dioxide and hydrogen sulfide. Introduction of sulfur dioxide caused heat to be liberated and hydrogen chloride came off, while the crystalline mass was gradually transformed into a liquid. When the whole mass had changed into liquid, the reaction was stopped. The β-alkoxyethoxyvinylphosphonyl chlorides were isolated from this liquid by fractionation.

In a general way the reaction leading to formation of the acid chlorides may be represented by the scheme:

$$ROCH_2-CH_2-O-CHCl-CH_2\cdot PCl_4\cdot PCl_5 + 2SO_2 \rightarrow$$

$$\rightarrow ROCH_2-CH_2-O-CH=CHPOCl_2 + 2SOCl_2 + POCl_3 + HCl$$

The same acid chlorides were synthesized by the action of water and carboxylic acids upon the products of addition of PCl_5 to monoalkylvinyl ethers of ethylene glycol according to the equations:

$$ROCH_2-CH_2-O-CHCl-CH_2\cdot PCl_4\cdot PCl_5 + 2H_2O \rightarrow$$

$$\rightarrow ROCH_2-CH_2-O-CH=CHPOCl_2 + POCl_3 + 5HCl$$

$$ROCH_2-CH_2-O-CHCl-CH_2\cdot PCl_4\cdot PCl_5 + 2CH_3COOH \rightarrow$$

$$\rightarrow ROCH_2-CH_2-O-CH=CH\cdot POCl_2 + POCl_3 + 2CH_3COCl + 3HCl.$$

β-Alkoxyethoxyvinylphosphonyl chlorides are colorless, transparent liquids, easily distillable in vacuum, rapidly decolorizing bromine water and permanganate, and hydrolyzable by water with formation of non-distillable and non-crystallizing syrups; the chlorides are soluble in all organic solvents. By this method the following compounds were prepared in yields of 90-97 % of the theoretical: The chlorides of β-methoxy ethoxyvinylphosphonic, and β-ethoxyethoxyvinylphosphonic, and β-n-butoxyethoxyvinylphosphonic acids.

The β-alkoxyethoxyvinylthiophosphonyl chlorides were prepared in the same conditions as for the synthesis of the β-alkoxyethoxyvinylphosphonyl chlorides. The only difference was that the action of hydrogen sulfide on the products of addition of PCl_5 to the monoalkylvinyl ethers was continued up to full transformation of the crystalline product into a liquid. After driving off the solvent and phosphorus thiochloride, the β-alkoxyethoxyvinylthiophosphonyl chlorides were isolated. Reaction scheme:

$$ROCH_2-CH_2-O-CHCl-CH_2PCl_4\cdot PCl_5 + 2H_2S \rightarrow$$
$$\rightarrow ROCH_2-CH_2-O-CH=CHPSCl_2 + PSCl_3 + 5HCl.$$

The chlorides of β-methoxyethoxyvinylthiophosphonic and β-n-butoxyethoxyvinylthiophosphonic acids were isolated in a yield of 76-86 % of the theoretical. The chlorides of β-alkoxyethoxyvinylthiophosphonic acids are pale yellow liquids they rapidly decolorize bromine water and permanganate and give a positive reaction for chlorine; they are hydrolyzed very slowly by water; they are easily soluble in common organic solvents. The constants and yields of the prepared β-alkoxyethoxyvinylphosphonyl and β-alkoxyethoxyvinylthiophosphonyl chlorides are set forth in the table.

Formula	B.p. in °C (p in mm mercury)	n_D^{20}	d_4^{20}	Yield in %
$CH_3O-CH_2-CH_2-O-CH=CHPOCl_2$	115 (2)	1,4991	1,3200	95
$C_2H_5O-CH_2-CH_2-O-CH=CHPOCl_2$	123 (2)	1,4920	1,2881	97
$n-C_4H_9O-CH_2-CH_2-O-CH=CHPOCl_2$	142 (2)	1,4869	1,2133	90
$CH_3O-CH_2-CH_2-O-CH=CHPSCl_2$	113 (2)	1,5413	1,3364	76
$C_2H_5O-CH_2-CH_2-OCH=CHPSCl_2$	120 (2)	1,5330	1,2887	85
$n-C_4H_9O-CH_2-CH_2-OCH=CHPSCl_2$	137 (2)	1,5100	1,2210	86

EXPERIMENTAL

β-Methoxyethoxyvinylphosphonyl chloride $CH_3-O-CH_2-CH_2-O-CH=CHPOCl_2$. In a three necked flask, fitted with mechanical stirrer, reflux condenser (with calcium chloride tube) and dropping funnel, were placed 150 ml dry benzene and 83.5 g (0.4 mole) finely pulverized PCl_5; with energetic stirring of the suspension, gradual addition was then made of 20.4 g (0.2 mole) benzene solution of ethylene glycol methylvinyl ether (b.p. 107.5 deg; n_D^{20} 1.4162), prepared by the method of Shostakovsky and Tyupaev [2]. Addition of ether was accompanied by heat liberation and by copious evolution of hydrogen chloride. After the whole amount of the ether had been added, the mixture formed two layers – the upper one of benzene and the lower one of an oily liquid. The latter crystallized completely after cooling. The next day, after heating for 30 min. on a water bath at 55-60°, the mixture was treated with sulfur dioxide until the crystalline mass had completely dissolved. The benzene, phosphorus oxychloride and thionyl chloride were driven off in the vacuum of a water jet pump. Fractionation of the residue yielded 42 g substance (95 % of the theoretical) with b.p. 115° (2 mm); n_D^{20} 1.4991; d_4^{20} 1.3200.

Found %: C 26.92; 27.20; H 4.27; 4.32; P 14.11; 14.17; Cl 32.61; 32.57
$C_5H_9O_3PCl_2$. Calculated %: C 27.39; H 4.10; P 14.15; Cl 32.42

β-Ethoxyethoxyvinylphosphonyl chloride $C_2H_5-O-CH_2-CH_2-O-CH=CHPOCl_2$. 24 g (0.2 mole) ethylene glycol monoethylvinyl ether (b.p. 123.7 deg; n_D^{20} 1.4014) was added with stirring to 83.5 g PCl_5 dissolved in 150 ml benzene. The following day the addition product was treated with sulfur dioxide until the crystalline product had changed into a liquid. Fractionation of the reaction mass yielded 46 g substance (97 % of the theoretical) with b.p. 123 deg (2 mm); n_D^{20} 1.4920; d_4^{20} 1.2881.

Found %: C 30.88; 30.84; H 4.65; 4.88; P 13.59; 13.44; Cl 30.43; 30.54
$C_6H_{11}O_3PCl_2$. Calculated %: C 30.90; H 4.72; P 13.30; Cl 30.47

β-n-Butoxyethoxyvinylphosphonyl chloride $n-C_4H_9-O-CH_2-CH_2-O-CH=CHPOCl_2$. 28.8 g (0.2 mole) ethylene glycol monobutylvinyl ether was added with stirring to a benzene suspension of PCl_5 consisting of 83.5 g PCl_5 and 150 ml benzene. The crystalline addition product was treated with sulfur dioxide until the whole of the crystalline mass had changed into liquid. Vacuum fractionation yielded 46.9 g acid chloride (90% of the theoretical) with b.p. 142° (2 mm); n_D^{20} 1.4869; d_4^{20} 1.2133.

Found %: P 11.82; 11.87; Cl 27.20; 27.47
$C_8H_{15}O_3PCl_2$. Calculated %: P 11.87; Cl 27.20

β-Methoxyethoxyvinylthiophosphonyl chloride $CH_3-O-CH_2-CH_2-O-CH=CHPSCl_2$. The synthesis was performed in the above-described apparatus. To a benzene suspension comprising 83 g PCl_5 and 150 ml benzene was added with stirring 20 g (0.2 mole) ethylene glycol monomethylvinyl ether (b.p. 107.5°; n_D^{20} 1.4162). The addition product was subjected to the action of hydrogen sulfide until the whole of the crystalline material had changed into liquid. Fractionation yielded 35.5 g substance (76% of the theoretical) with b.p. 113° (2 mm); n_D^{20} 1.5413; d_4^{20} 1.3364.

Found %: C 25.82; 26.02; H 3.44; 3.75; P 12.89; 13.16
$C_5H_9O_2PSCl_2$. Calculated %: C 25.53; H 3.82; P 13.19

β-Ethoxyethoxyvinylthiophosphonyl chloride $C_2H_5-O-CH_2-CH_2-O-CH=CHPSCl_2$. 23.2 g (0.2 mole) ethylene glycol monoethylvinyl ether (b.p. 123.7 °; n_D^{20} 1.4104) was added to a suspension of 82.5 g PCl_5 in 130 ml benzene. The following day the crystalline addition product was treated with hydrogen sulfide until the whole of the crystalline mass had changed into liquid. Vacuum fractionation yielded 42.6 g substance (85 % of the theoretical) with b.p. 120 deg (2 mm); n_D^{20} 1.5330; d_4^{20} 1.2887.

Found %: C 29.10; 29.19; H 4.16; 3.94; P 12.55; 12.46
$C_6H_{11}O_2PSCl_2$. Calculated %: C 28.91; H 4.41; P 12.44

β-n-Butoxyethoxyvinylthiophosphonyl chloride n-$C_4H_9-O-CH_2-CH_2-O-CH=CHPSCl_2$. To 83 g (0.4 mole) PCl_5 and 150 ml benzene was added, with stirring, 28.8 g ethylene glycol n-butylvinyl ether (b.p. 159-160°; n_D^{20} 1.4210). The following day the crystalline addition product was treated with hydrogen sulfide. Fractionation in vacuum yielded 47 g substance (86% of the theoretical) with b.p. 137 °(2 mm); n_D^{20} 1.5100; d_4^{20} 1.2210.

SUMMARY

Reaction of PCl_5 with alkylvinyl ethers of ethylene glycol yielded the chlorides of: β-methoxyethoxyvinylphosphonic, β-ethoxyethoxyvinylphosphonic, and β-n-butoxyethoxyvinylphosphonic acids; also the chlorides of β-methoxyethoxyvinylthiophosphonic, β-ethoxyethoxyvinylthiophosphonic and β-n-butoxyethoxyvinylthiophosphonic acids.

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Received September 21, 1953

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DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 4. ARYLVINYLPHOSPHONYL CHLORIDES

K. N. Anisimov

We have previously described the reaction of addition of phosphorus pentachloride to vinyl ethers and the synthesis of β-alkoxy(phenoxy)-vinylphosphonyl chlorides [1]. We made a similar investigation of unsaturated compounds of the aromatic series – styrene, indene and phenylacetylene. As is known, Harnist [2] added phosphorus pentachloride to styrene, diphenylethylene, isobutylene and phenylacetylene. Bulle reacted phosphorus pentachloride with indene [3]. Bergman and Bondi [4,5,6,7] studied the addition of phosphorus pentachloride to unsaturated compounds of the aromatic series.

All these investigators subjected to hydrolysis the products of addition of phosphorus pentachloride to unsaturated hydrocarbons and obtained unsaturated phosphonic acids. They did not carry out other investigations with the addition products.

On the basis of our research we concluded that if the products of addition of phosphorus pentachloride to styrene, phenylacetylene, and indene were to be reacted with sulfur dioxide, formation should take place of the corresponding chlorides of the unsaturated phosphonic acids which can serve as starting materials for the synthesis of diverse derivatives of unsaturated phosphonic acids. The first experiments showed the correctness of our conclusion. Reactions were performed in the following conditions. In an Erlenmeyer flask were placed dry benzene and thoroughly pulverized phosphorus pentachloride; the flask was then closed with a cork through which was inserted a calcium chloride tube and a dropping funnel. The unsaturated compound was added in portions from the dropping funnel with stirring. The reaction took place with liberation of heat and with evolution of hydrogen chloride. At the end of the reaction, a crystalline mass had formed and this was left overnight. The following day the addition product was treated with sulfur dioxide until the solid mass was completely changed into a liquid. The benzene was then driven off and the residue was at first kept in the vacuum of a water jet pump on a water bath until the hydrogen chloride had been completely removed, and then fractionated in vacuum.

In this way β-phenylvinylphosphonyl chloride was obtained in a yield of 98-99% of the theoretical, and indenyl-2-phosphonyl chloride in slightly lower yield. The synthesized acid chlorides are crystalline substances with an acid chloride odor, readily soluble in ether, chloroform, benzene and other organic solvents; they react slowly with cold water.

The preparation of the chlorides of arylvinylphosphonic acids may be expressed by the scheme:

$$RCH{=}CH_2 + 2PCl_5 \rightarrow RCHCl - CH_2PCl_4 \cdot PCl_5,$$

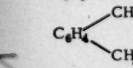
$$RCHCl - CH_2PCl_4 \cdot PCl_5 + 2SO \rightarrow RCH{=}CHPOCl_2 + POCl_3 + 2SOCl_2 + HCl.$$

β-Chlorophenylvinylphosphonyl chloride is obtained in quantitative yield by the same method as described above, except that hydrogen chloride was not split off from the product of addition of phosphorus pentachloride to phenylacetylene. β-Chlorophenylvinylphosphonyl chloride is a thick, transparent liquid, soluble in common organic solvents, slowly hydrolyzed by cold water and more energetically by hot. The synthesis of β-chlorophenylvinylphosphonyl chloride may be represented by the equations:

$$C_6H_5C{\equiv}CH + 2PCl_5 \rightarrow C_6H_5CCl{=}CHPCl_4 \cdot PCl_5,$$

$$C_6H_5CCl{=}CH_2PCl_4 \cdot PCl_5 + 2SO_2 \rightarrow C_6H_5CCl{=}CHPOCl_2 + POCl_3 + 2SOCl_2.$$

β-Arylvinylphosphonyl chlorides were also prepared in this investigation, using the calculated amount of water in place of sulfur dioxide. The constants and yields of the prepared acid chlorides are set forth in the table.

Formula	B.p. in °C (p in mm mercury column)	n_D^{20}	d_4^{20}	Yield in %
$C_6H_5CH{=}CHPOCl_2$	M.p. 71-72°	—	—	96
	M.p. 73-74°	—	—	62
$C_6H_5CCl{=}CHPOCl_2$	142.5-143.5° (1)	1.6175	1.4675	80

EXPERIMENTAL

β-Phenylvinylphosphonyl chloride $C_6H_5CH{=}CHPOCl_2$. To 104 g phosphorus pentachloride in 150 ml dry benzene was gradually added, with stirring and water cooling, 26.2 g styrene dissolved in 50 ml benzene. Addition of the styrene resulted in formation of a dense crystalline mass. The next day a stream of sulfur dioxide was passed into the reaction mixture until the crystalline mass had completely changed into liquid. Hydrogen chloride was copiously evolved by the reaction mixture during introduction of the sulfur dioxide. The mixture was then subjected to vacuum fractionation to give 55 g (96% of the theoretical) of acid chloride: b.p. 139° (2 mm); M.p. 71-72°.

	Found %:	C 43.30; 43.19;	H 3.28, 3.32; Cl 31.86, 32.20.
$C_8H_7OCl_2P$.	Calculated %:	C 43.43;	H 3.16; Cl 32.12

β-Phenylvinylphosphonyl chloride is a white crystalline substance with an acid chloride odor, soluble in ordinary organic solvents and slowly hydrolyzing in water.

Indenyl-2-phosphonyl chloride . In a three-necked flask, fitted with stirrer, reflux condenser and dropping funnel, were placed 200 ml dry benzene and 83 g finely pulverized phosphorus pentachloride. To the suspension was added 24 g indene with energetic stirring dissolved in 20 ml benzene. A voluminous crystalline mass had formed when the whole of the indene had been added. The following day a further 50ml benzene was added, the whole was stirred and heated to 65-70°; a stream of sulfur dioxide was then passed through until the crystalline mass had been completely changed into liquid. After the benzene, phosphorus oxychloride and thionyl chloride had been driven off, the residue was kept on a boiling water bath in the vacuum of a water jet pump for removal of the hydrogen chloride. Vacuum fractionation of the residue yielded 30 g (62% of the theoretical) substance with b.p. 133 deg (1 mm); M.p. 73-74°.

	Found %:	C 46.14, 46.01;	H 2.99, 3.20; P 13.22, 13.12
$C_9H_7OCl_2P$	Calculated %:	C 46.35;	H 3.00 P 13.30

Indenyl-2-phosphonyl chloride is readily soluble in many organic solvents, and is slowly hydrolyzed by water.

β-Chlorophenylvinylphosphonyl chloride $C_6H_5CCl{=}CHPOCl_2$. To a suspension of 83 g phosphorus pentachloride in 150 ml dry benzene was gradually added 20.4 g phenylacetylene with shaking and water cooling. Heat was developed during the reaction. The following day sulfur dioxide was passed into the crystalline mass until the latter was completely transformed into a liquid. The mixture was then fractionated in vacuum. The solvent, phosphorus oxychloride and thionyl chloride were driven off in a low vacuum (water jet pump) and the residue twice fractionated at 1 mm. Yield 44.5 g (87% of the theoretical) of β-chlorophenylvinylphosphonyl chloride with b.p. of 142.5-143.5° (1 mm); n_D^{20} 1.6175; d_4^{20} 1.4675.

	Found %:	P 12.11, 12.40;	C 37.44, 37.21; H 2.67, 2.40; Cl 41.53, 41.40
$C_8H_6OPCl_3$.	Calculated %:	P 12.15;	C 37.57; H 2.34; Cl 41.68

β-Chlorophenylvinylphosphonyl chloride is a colorless, viscous liquid, faintly fuming in the air, slowly hydrolyzed by water; it has the odor of an acid chloride and is soluble in many organic solvents.

SUMMARY

For the first time a method was developed for the preparation of chlorides of β-arylvinylphosphonic acids.

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Received September 24, 1953

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SYNTHESIS OF ESTERS OF PHOSPHONIC ACIDS CONTAINING HETEROCYCLIC RADICALS

COMMUNICATION 4. ESTERS OF PHOSPHONIC ACIDS CONTAINING ISOXAZOLE AND QUINOXALINE RADICALS

B. A. Arbuzov and V. M. Zoroastrova

In previous communications we described the results of syntheses of esters of phosphonic acids containing thiazole radicals [1], heterocyclic radicals with one and two atoms of oxygen in the ring [2], and the piperidine radical [3]. In a continuation of these investigations we have studied esters of phosphonic acids containing other heterocycles. In the present paper we present data for the synthesis of esters of phosphonic acids containing isoxazole and quinoxaline radicals.

Action of triethylphosphite upon 3-chloromethylisoxazole at 150-155° gave the ethyl ester of 3-isoxazolylmethylphosphonic acid in the form of a viscous, colorless liquid in the yield of 59.1 % of the theoretical; b.p. 152-153° (7-7.5 mm); d_0^{20} 1.1892; n_D^{20} 1.4650; Found MR 50.93; Calculated MR 50.72.

Reaction of molar amounts of trimethyl phosphite and 3-chloromethylisoxazole gave in lower yield (21% of the theoretical) the methyl ester of 3-isoxazolylmethylphosphonic acid with b.p. 142-145° (5 mm); d_0^{20} 1.2744; n_D^{20} 1.4670; Found MR 41.64; Calculated MR 41.49.

Similarly from tri-n-propyl phosphite and 3-chloromethylisoxazole at about 160° was obtained n-propyl 3-isoxazolylmethanephosphonate with b.p. 150-152° (2.5 mm); d_0^{20} 1.1541; n_D^{20} 1.4675; Found MR 59.47; Calculated MR 59.95. Yield 65.5%.

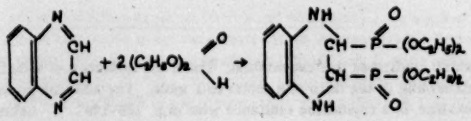
Ethyl 3-isoxazolylmethanephosphonate was obtained by the action of sodium diethylphosphite on 3-chloromethylisoxazole. The yield of ester obtained by this method was considerably lower than the yield of ester obtained by reaction of triethyl phosphite with 3-chloromethylisoxazole and was 17% of the theoretical.

The esters of 3-isoxazolylmethanephosphonic acid are viscous liquids soluble in ether, benzene, alcohol and water. An attempt to prepare the free 3-isoxazolylphosphonic acid by hydrolysis of the esters with hydrochloric acid (1:1) was unsuccessful due to resinification of the products. Alkaline hydrolysis of the esters gave the phosphonic acid in the form of a viscous, non-crystallizing syrup, from which the barium salt was subsequently prepared. The second part of the research was devoted to the study of the reaction of trialkyl phosphites with halogenated derivatives of quinoxaline.

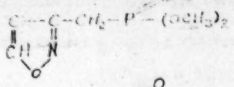
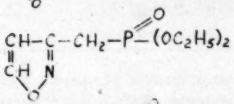
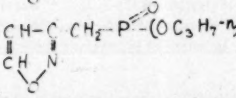
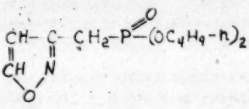
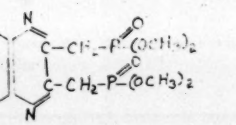
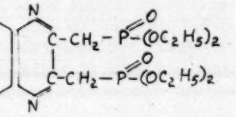
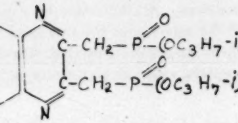
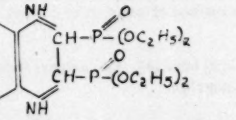
Condensation of dibromodiacetyl with o-phenylenediamine in ethanolic solution gave 2,3-di(ω-bromomethyl)-quinoxaline. Reaction of the latter with trimethyl, triethyl and triisopropyl phosphites enabled synthesis of the corresponding esters of 2,3-di(ω-phosphonomethyl)-quinoxaline. All the esters are crystalline substances, soluble in organic solvents and in water. Saponification of the esters gave the free acid. It is interesting to note that on acting with sodium diethyl phosphite on 2,3-di(ω-bromomethyl)-quinoxaline, the anticipated reaction product was not isolated. The constants of the prepared esters of phosphonic acids are set forth in the table.

The above method can serve for the preparation of esters of phosphonic acids containing the phosphonic group in the side chain. For the preparation of esters of phosphonic acids containing the phosphonic group directly attached to a heterocyclic nucleus, we made use of Pudovik's method of addition of dialkyl phosphorous acids at the active double bond.

It is known from literature data that quinoxaline adds on at the C=N bond [4]. By analogy, therefore, we should expect diethyl phosphorous acid to add on in this way to quinoxaline.



TABLE

Prep. No.	Formula	B.p. in °C (p in mm mercury)	d_4^{20}	n_D^{20}	MR Found	MR Calculated
1		142-145 (5)	1.2744	1.4670	41.60	41.49
2		152-153 (7-7.5)	1.1892	1.4650	50.93	50.72
3		150-152 (2.5)	1.1541	1.4675	54.49	69.20
4		155-156 (1)	1.0750	1.4575	69.77	69.20
5		M.p. 115-116	Colorless prisms from ether			
6		92-93	From n-heptane			
7		102-103	From n-heptane			
8		168-170				

Experiments were carried out which confirmed this expectation. Under the influence of sodium ethoxide, sodium diethyl phosphite adds on to quinoxaline in the ratio of 2 moles to 1 mole. The addition product, 1,4-dihydro-2,3-di(diethylphosphono)-quinoxaline, is a crystalline substance with m.p. 168-170°. Substitution of the hydrogens in the 2-and 3-positions of quinoxaline by methyl groups hinders the addition of diethylphosphorous acid, and the reaction does not take place.

EXPERIMENTAL

1. Action of 3-chloromethylisoxazole on triethyl phosphite. 10 g triethyl phosphite was placed in a small Arbuzov flask and heated on an oil bath to 120-125° inside a small flask. Dropwise addition was made to the heated triethyl phosphite of 7.01 g (1 mole per mole triethyl phosphite) 3-chloromethylisoxazole, the heating being gradually intensified during the operation. Reaction commenced at 150-155° (evolution of ethyl chloride). This temperature was maintained for an hour. The volume of the reaction mixture gradually contracted. Vacuum distillation yielded 7.8 g (59% of the theoretical) of product boiling at 152-153° (7-7.5 mm); d_4^{20} 1.1892; n_D^{20} 1.4640; Found MR 50.93; calculated MR 50.72. The colorless, fairly viscous liquid is soluble in ether, benzene, ethanol and water.

Found %: P 14.14
Calculated %: P 14.14 $C_8H_{14}O_4PN$

2. Action of 3-chloromethylisoxazole on trimethyl phosphite. The reaction procedure was similar to that described above. Reactants were 6.3 g trimethyl phosphite and 5.83 g 3-chloromethylisoxazole. The trimethyl phosphite which distilled over was returned to the reaction mixture. After heating for an hour, the reaction products were fractionated in vacuum to give 2 g (21%) viscous, faint yellow liquid. Further heating led to serious decomposition of the reaction products. B.p. 142-145° (5 mm); d_4^{20} 1.2744; n_D^{20} 1.4670; Found MR 41.60; calculated MR 41.49. The product dissolves readily in organic solvents. Unlike the first product it is also easily soluble in water.

Found %: P 15.73
Calculated %: P 16.22. $C_6H_{10}O_4PN$

3. Action of 3-chloromethylisoxazole on tri-n-propyl phosphite. 5.2 g tri-n-propyl phosphite and 3 g 3-chloromethylisoxazole were heated in a small distillation flask on an oil bath. n-Propyl chloride (b.p. 46.5°) started to come off at about 160°. Heating was continued for an hour. Distillation in vacuum gave about 4 g (65.5%) of viscous, colorless liquid boiling at 150-152° (2.5 mm); d_4^{20} 1.1541; n_D^{20} 1.4675; Found MR 59.47; Calculated MR 59.95. The product is soluble in ether, benzene, chloroform and ethanol. The solubility in water is somewhat lower than the solubility of the ethyl ester.

Found %: P 12.42
Calculated %: P 12.54 $C_{10}H_{18}O_4PN$

4. Action of 3-chloromethylisoxazole on sodium diethyl phosphite. To an ethereal solution of sodium diethyl phosphite, prepared from 0.9 g Na and 6.21 g $(C_2H_5O)_2POH$ (the theoretical amount is 5.21 g), was added 4.33 g 3-chloromethylisoxazole. The solution was refluxed for 6 hours. Separation of the precipitated sodium chloride, which came down in a colloidal form, was facilitated by addition of a small amount of water. After filtration, the ethereal solution was dried with calcium chloride and distilled in vacuum. Yield 1.4 g (17%) product with b.p. 148° (5 mm); n_D^{20} 1.4625.

Hydrolysis of reaction products. 0.5 g ethyl isoxazolylmethanephosphonate was heated with dilute hydrochloric acid at 120-125° for 5 hours. Evaporation on the water bath with repeated addition of water yielded a dark resinous residue which did not crystallize after prolonged standing in a desiccator over sulfuric acid. Hydrolysis of the n-propyl ester with hydrochloric acid gave a similar result. No pure product of hydrolysis was isolated.

Alkaline hydrolysis. 1.9 g ethyl ester was heated to boiling with 1 g NaOH in 50 ml water for 4.5 hours. The solution was neutralized with hydrochloric acid and evaporated to dryness. The residue was extracted with absolute ethanol. Evaporation of the alcohol left a non-crystallizing, viscous liquid. This was dissolved in water and boiled with barium carbonate. The solution of barium salt was digested with animal charcoal and evaporated to dryness on a water bath. The dried, slightly yellowish residue was analyzed for barium.

Found %: Ba 47.08
Calculated %: Ba 46.03. $C_4H_4O_4NPBa$

5. Action of 3-chloromethylisoxazole on tri-n-butyl phosphite. 3.9 g 3-chloromethylisoxazole and 8.4 g tributyl phosphite (1 mole to 1 mole ester) were heated in an Arbuzov flask. Reaction commenced at 170° (temperature of the mixture). The mixture was heated at 170-180° for 2 hours and at 180-195° for 1 hour. 2 g n-butyl chloride was separated (b.p. 77-79°; n_D^{20} 1.4065). Distillation of the reaction products gave a substance with b.p. 155-156° (1 mm); 3.4 g (35.5% of the theoretical); d_4^{20} 1.0750; n_D^{20} 1.4575; Found MR 69.77; calculated MR 69.19.

6. Reaction of 2,3-di(ω-bromomethyl)-quinoxaline with trimethyl phosphite. 2,3-di(ω-bromomethyl)-quinoxaline was prepared by condensation of dibromodiacetyl with o-phenylenediamine in ethanolic solution [5]. After crystallization from ethanol with use of active carbon, the m.p. was 151-152° (literature 150°). 2 g 2,3-di-(ω-bromomethyl)-quinoxaline and 1.65 g trimethyl phosphite in 10 ml dry benzene were boiled for 1.5 hours. After driving off the greater part of the benzene, the reaction products were further heated at 130° for 5 min. After cobling, the liquid product was poured on to a watch glass. Addition of n-heptane and rubbing with a glass rod caused crystallization. Yield 1.7 g (70.8%) crystals with a wide melting point. Three crystallizations from ether gave prisms melting at 115-116° to a yellow liquid. The prisms are soluble in benzene, ether, methanol and ethanol, also in water.

Found %: P 16.43
Calculated %: P 16.57 $C_{14}H_{20}O_6P_2N_2$.

Hydrolysis of the ester. 0.64 g ester was heated in a sealed tube with 15 ml dilute (1:1)hydrochloric acid at 100° for 7 hours. The contents of the tube were evaporated in a small beaker on a water bath with repeated additions of water until the hydrochloric acid had been completely removed. The product was purified by recrystallization from water with addition of active carbon. Light-yellow crystals; they darkened when heated above 200° and melted at about 234° with decomposition into a dark liquid.

Found %: P 19.06
Calculated %: P 19.49 $C_{10}H_{12}O_6P_2N_2$.

7. Reaction of 2,3-di(ω-bromomethyl)-quinoxaline with triethyl phosphite. 1.5 g 2,3-di(ω-bromomethyl)-quinoxaline and 1.67 g triethyl phosphite were heated in 10 ml dry benzene for 5 hours. After part of the benzene had been driven off, 3-4 ml n-heptane was added to the flask. A white precipitate immediately came down—1 g (50 %). This was recrystallized from n-heptane, m.p. 92-93°. Its properties resembled those of the preceding product.

Found %: P 14.43
Calculated %: P 14.41 $C_{18}H_{28}O_6P_2N_2$.

Hydrolysis of the ethyl ester. Hydrolysis of the product was effected as before by heating with dilute hydrochloric acid in a sealed tube at 110-115° for 5 hours. An acid was obtained which darkened when heated to 210° and melted to a dark liquid on further heating.

8. Reaction of 2,3-di(ω-bromomethyl)-quinoxaline with triisopropyl phosphite. A mixture of 1.5 g of the dibromide and 2.08 g phosphite in 10 ml dry benzene was heated to the boil in an Arbuzov flask for 2 hours. The benzene was then driven off and the residue heated for 5 min. at 140°. Addition of n-heptane brought down crystals in the form of colorless needles; yield 1.2 g (51.8%). After recrystallization from n-heptane the product melted at 102-103°; readily soluble in benzene, ether, ethanol, and methanol; soluble in water.

Found %: P 12.83
Calculated %: P 12.75 $C_{22}H_{36}N_2P_2O_6$.

9. Reaction of 2,3-di(ω-bromomethyl)-quinoxaline with tri-n-propyl phosphite. 1.5 g 2,3-di(ω-bromomethyl)-quinoxaline and 2.08 g tri-n-propyl phosphite were heated in 10 ml dry benzene for 3 hours. After working up in the usual way, the product did not crystallize. After long standing in a small open beaker, the product remained in the form of a thick liquid, soluble in organic solvents and water.

10. Reaction of 2,3-di(ω-bromomethyl)-quinoxaline with sodium dimethyl phosphite.

Experiment 1. An ethereal solution of 2,3-di(ω-bromomethyl)-quinoxaline and sodium dimethyl phosphite (1 mole of quinoxaline to 2 moles of sodium salt) was refluxed on a water bath for 3 hours. The quinoxaline derivative was recovered unchanged.

Experiment 2. A similar experiment was carried out in ligroine solution (b.p. 80-110°). After the precipitated sodium chloride had been filtered off and the ligroine distilled off from the filtrate, the reaction product did not crystallize and remained in the form of a viscous, non-crystallizing liquid with a brown color. Hydrolysis of this liquid with dilute hydrochloric acid led to resinification.

11. Reaction of quinoxaline with diethylphosphorous acid. Quinoxaline [6] was prepared by condensation of o-phenylenediamine with the bisulfite compound of glyoxal (m.p. 33-35°). In a small Arbuzov flask were placed 3.6 g diethylphosphorous acid and 1.7 g quinoxaline (2 moles acid to 1 mole quinoxaline). To the resultant solution was added 8-10 drops of an ethanolic solution of sodium ethoxide. The reaction mixture was heated on a water bath, during which process the color changed from light-yellow to a darker shade. After 1.5 hours the

contents of the flask had solidified. 4 g (approx 77 %) crystals was filtered off. After washing with ligroine they melted at 150-150°. Three recrystallizations from benzene with activated carbon gave fine, colorless hairs with m.p. 168-170°; readily soluble in ether, ethanol, chloroform and benzene; soluble in water.

Found %: P 15.75; 15.83
Calculated %: P 15.26. $C_{16}H_{28}N_2P_2O_6$.

Hydrolysis of the product with hydrochloric acid. 0.45 g product was heated in a sealed tube with 15 ml 10% hydrochloric acid at 100°. After a short period the product acquired a dark cherry-red color. Heating was continued for an hour. Evaporation of the products of hydrolysis on a water bath gave a non-crystallizing, reddish-brown mass.

Alkaline hydrolysis. 0.4 g substance was digested with 0.2 g NaOH in 25 ml water for 3 hours. After neutralization, evaporation on a water bath and boiling with active carbon, a resinous product was obtained.

12. Reaction of 2,3-dimethylquinoxaline with dimethyl- and diethylphosphorous acids. 2 g 2,3-dimethylquinoxaline and 3.4 g dimethylphosphorous acid were heated in a small Arbuzov flask with 8 drops of sodium methoxide. At the start the colorless solution became dark cherry-red. On intense cooling with snow and salt the mass did not crystallize; on standing it turned dark-blue and remained thus for a long period. Attempts to distil in vacuum likewise did not give the desired results (the substance decomposed). The reaction product could not be isolated in the pure form. Diethylphosphorous acid did not react at all in these conditions with 2,3-dimethylquinoxaline. After 5 hours' heating of the mixture in a boiling water bath, the starting substances were recovered unchanged.

SUMMARY

1. Reaction of sodium dialkyl phosphite and of trialkyl phosphite with 3-chloromethylisoxazole gave esters of phosphonic acids containing the isoxazole ring.

2. Reaction of trialkyl phosphites with 2,3-di(ω-bromomethyl)-quinoxaline led to the methyl, ethyl and isopropyl esters of 2,3-di(phosphonomethyl)-quinoxaline.

3. The phosphonic ester could not be isolated after reaction of sodium diethyl phosphite with 2,3-di-(ω-bromomethyl)-quinoxaline.

4. Diethylphosphorous acid adds on to quinoxaline under the influence of sodium alcoholate to form 1,4-dihydro-2,3-di(diethylphosphono)-quinoxaline.

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Received June 19, 1953

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DIPOLE MOMENTS OF SOME DERIVATIVES OF ETHYLPHOSPHONOUS AND ETHYLPHOSPHONIC ACIDS

B. A. Arbuzov and T. G. Shavsha-Tolkacheva

The monoesters of ethylphosphonous acid constitute an interesting group of derivatives of pentavalent phosphorus, which in their structure and the distribution of the dipole moments of the individual bonds are reminiscent of dialkyl esters of phosphorous acid and differ from the latter in that one OR group is replaced by a C_2H_5 group, due to which the monoesters of ethylphosphonous acid only contain one irregular alkoxy group.

We have determined the dipole moments of the following monoesters of ethylphosphonous acid, which were first synthesized by one of us and Rizpolozhensky [1], and we obtained the values of dipole moments set forth in Table 1.

TABLE 1

No.	Formula	Dipole moment in D	No.	Formula	Dipole moment in D
1	$C_2H_5-P(=O)(H)-OCH_3$	3.17	7	$C_2H_5-P(=O)(H)-OC_6H_{13}$	3.36
2	$C_2H_5-P(=O)(H)-OC_2H_5$	3.48	8	$C_2H_5-P(=O)(H)-OC_7H_{15}$	3.31
3	$C_2H_5-P(=O)(H)-OC_3H_7$-n	3.37	9	$C_2H_5-P(=O)(H)-OC_8H_{17}$	3.27
4	$C_2H_5-P(=O)(H)-OC_3H_7$-i	3.34	10	$C_2H_5-P(=O)(H)-OC_9H_{19}$	3.34
5	$C_2H_5-P(=O)(H)-OC_4H_9$-n	3.41	11	$C_2H_5-P(=O)(H)-OC_{10}H_{21}$	3.42
6	$C_2H_5-P(=O)(H)-OC_4H_9$-i	3.38			

We see from Table 1 that the dipole moments of monoesters of ethylphosphonous acid vary from 3.17 to 3.48 D and that the mean value for the series is 3.35 D. It is seen that the mean value of the dipole moments of the monoesters of ethylphosphonous acid (3.35 D) is slightly higher than that for the series of dialkylphosphorous acids (2.91 D). The dipole moment of the molecule of a monoester of ethylphosphonous acid is the resultant of the dipole moments of the P=O, P→O, H→P, R→O bonds and of the P→C bond. The molecule of the monoester contains one irregular group which can rotate around the P–O bond.

We have calculated the dipole moments of molecular models of rigid structures and the dipole moment of a molecule with free rotation of the OH group round the P–O bond. Comparison of the dipole moments calculated for the molecular models with the experimentally determined value of the dipole moment shows that the dipole moment of the rigid structure B (Fig. 1) is 1.61 D and differs markedly from the experimentally found magnitude. The dipole moments of models C and A exceed the experimentally found magnitude by 0.2 and 0.1 D, while the dipole moment of the molecule of the monoester with free rotation of the OR group is 3.32 D and nearly exactly corresponds to the experimentally found value of 3.35 D.

Fig. 1.

In the calculation of the dipole moments of rigid models and of a molecule with free rotation of the OR group, we assumed the following values for the valence angles: O = P − O, 118-119°; O−P−C angle equal to O−P−H angle and equal to 100°; we also assumed the following values for the dipole moments of individual bonds: P = O 3,5 D; P ⟶ O 1,2 D; R ⟶ O 1,12 D; H ⟶ P 0,55 D· P ⟶ C 0,8 D [2].

We calculated the interatomic distances of models of the molecule of monoester with allowance for the radius of the spheres of action of the van der Waals forces and we reached the conclusion that free rotation of the OR groups round the PO bond is possible in the molecule of the monoester, since during rotation the spheres of action of the van der Waals forces of the methyl and methylene groups are not superimposed. The interatomic distance of the P−O bond is equal to 1,76 A; that of the R−O bond 1,43 A; that of the P−H bond 1,47 A; and that of the P−C bond 1,87 A. Consequently for monoesters of ethylphosphonous acid we can propose a pyramidal structure with a O = P−O angle of 118°, and an O−P−C angle equal to the O−P−H angle and equal to 100°, with free rotation of the OR group round the P−O bond; the dipole moment of the P−C bond is 0,8 D and is directed from the phosphorus to the carbon.

The direction of the dipole moment of the P−C_2H_5 bond from phosphorous to carbon is retained in esters of ethylphosphonous acid, the structure and arrangement of the dipole moments of the individual bonds of which are reminiscent of those in esters of thiophosphoric acid and they differ from the latter in that one alkoxy group is replaced by an ethyl group; esters of ethylthiophosphonic acid contain only two irregular alkoxy groups which are able to rotate round the P−O bond.

A study of $P_4O_6S_4$ by the electron diffraction method gave a value of 101,5° . ± 1° for the O−P−O angle, and a value of 116,5° [3] for the O−P = S angle. On the basis of these results for esters of thiophosphoric acid a pyrimidal structure was proposed with a S = P−O angle of 118-119°, and a O−P−O angle of 100°. For esters of ethylphosphonic acid we also assume a pyramidal structure with a O−P−O angle equal to the O−P−C angle and equal to 100°; also a S−P−O angle equal to 118-119°, since substitution of an alkoxy group by ethyl does not introduce great difference in the geometrical structure of the molecule and cannot seriously influence the magnitude and direction of the dipole moments of the individual bonds.

We only had two esters of ethylthiophosphonic acid available for measurement: the ethyl and n-propyl esters prepared by one of us and Rizpolozhensky [4]. The dipole moments of the esters of ethylthiophosphonic acid are set forth in Table 2.

TABLE 2

No.	Formula	Dipole moment in D
1	$(C_2H_5O)_2-P(=S)-C_2H_5$	3,22
2	$(C_3H_7O)_2-P(=S)-C_2H_5$-n	2,95

The dipole moment of the n-propyl ester is a little lower, probably due to inadequate purity of the sample, as reflected in the molecular refraction: found MR 57,80; calculated MR 57,08.

We calculated the dipole moments of molecular models of rigid structure and with allowance for rotation of the OR group round the P−O bond. On the basis of a comparison of the experimentally found values of the dipole moments with those calculated for various molecular models, it can be concluded that the dipole moments of the rigid models are 4,20 D for model A_1, 0,77 D for model B_1 and 2,42 D for model C_1 (Fig. 2.); these differ considerably from the values found. The dipole moment of a molecule calculated on the assumption of possible free rotation of two OR groups round the P = O bonds is equal to 2,98 D and comes nearest to the experimentally determined value. The following values of the dipole moments of the individual bonds were used in the calculation of the dipole moments of molecular models: P=S 3,6 D; P ⟶ O 1,2 D; R ⟶ O 1,12 D [5]. The dipole moment of the P ⟶ C bond was taken as 0,8 D, and the direction from phosphorus to carbon.

For the explanation of the possibility of free rotation of the two OR groups round P−O bonds we considered the interatomic distances of the individual models with free rotation, allowing for the radius of action of the van der Waals forces of the methyl and methylene groups. For the esters of ethylthiophosphonic acid, model A_1 has

the least overlapping of the spheres of action of the van der Waals forces of the methyl groups and therefore this model is highly improbable for esters of ethylthiophosphonic acid. Models B_1 and C_1 are possible for esters of ethylthiophosphonic acid since they do not have overlapping of the spheres of action of the van der Waals forces, and hence esters of ethylthiophosphonic acid can only execute anoscillatory movement with an amplitude of 180° at which model C_1 passes into model B_1 and again into C_1. The dipole moment of the molecular model of the ester of ethylthiophosphonic acid calculated for synchronous oscillation of two OR groups round the P=O bond, when the OR groups successively occupy the positions indicated in models C_1 and B_1 and again in C_1, is equal to 1,86 D and differs by 1,00 D from the experimentally found value.

This considerable difference between the experimental and the calculated dipole moment, when assuming paired synchronous oscillation of two OR groups round the P–O bond, suggested to us the possibility of molecular models of esters of ethylthiophosphonic acid in which both OR groups rotate round the P–O bonds synchronously, but during the movement they occupy a different position in respect to the plane of the P = O bond.

The following four models (Fig. 3.) may be advanced for esters of ethylthiophosphonic acid: A_2, B_2, C_2, D_2.

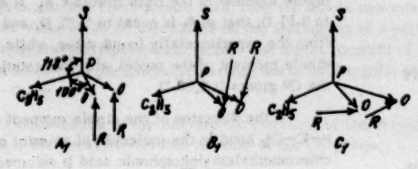


Fig. 2

The dipole moment of model A_2 proved to be 1.57 D, that of model B_2 3,27 D, that of C_2 3.53 D and that of D_2 1.74 D. The dipole moment of a molecule of ester of ethylthiophosphonic acid, calculated on the above assumption of synchronous rotation of the OR groups round the P–O bond, as a mean arithmetic μ of models A_2, B_2, C_2, and D_2 is equal to 2.53 D and differs by 0.4 D from the experimental value.

On the basis of the above considerations it may be suggested that completely free rotation is impossible in esters of ethylthiophosphonic acid, but that there is a possibility of synchronous rotation around the P–O bond to the extent of 360°, as represented for the series of models A_2, B_2, C_2, D_2.

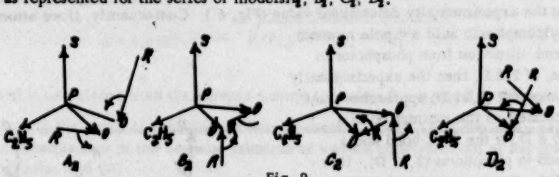


Fig. 3

Continuing our studies of the dipole moments of organophosphorus compounds, it seemed of interest to us to measure the dipole moments of esters of trichloromethylethylphosphonic acid in order to determine the magnitude and direction of the dipole moment of the P–C_2H_5 bond in esters of trichloromethylethylphosphonic acid. In respect of their structure and the distribution of dipole moments of the individual bonds, the esters of trichloromethylethylphosphonic acid resemble the esters of monoalkylphosphonic acid, only differing from the latter by the fact that one OR group in the esters of monoalkylphosphonic acids is substituted by the trichloromethyl radical CCl_3.

For esters of monoalkylphosphonic acids we assumed a pyramidal model with a O=P–O angle of 118-119° and a O=P–C angle of 100°, since the electron diffraction data in the literature indicate that the O–P–O angle is equal to the O–P–C angle and each is equal to 100° [2]. For esters of trichloromethylethylphosphonic acid we likewise assumed a pyramidal structure with O–P–O angles equal to 118° and O–P–C angles equal to 100°.

The resultant moment of the molecule of an ester of trichloromethylethylphosphonic acid is made up from the dipole moments of the P = O bond, the P ⟶ O bond, the R ⟶ O bond, the P–C_2H_5 bond and the P–CCl_3 bond. The dipole moment of the P = O bond is assumed to be 3.5 D, that of the P–O bond 1.2 D, that of the R–O bond 1,12 D. By analogy with esters of monoalkylphosphonic acids, the dipole moment of the P–C_2H_5 bond is assumed to be 0.8 D and its direction from phosphorus to carbon. The dipole moment of the P–CCl_3 bond is compounded from the dipole moment of the P–C bond and the moment of the C–Cl_3 bond. We assume a value of 0.8 D for the moment of the P – C bond, and we assume the moment of the C – Cl_3 bond to be equal to that of the C – Cl bond, i.e., 1.5 D. Since both the dipole moments lie on one straight line, the dipole moment of the P – C – Cl_3 bond is equal to 2.3 D.

We measured the dipole moments of three esters of trichloromethylethylphosphonic acid: the methyl, ethyl and propyl esters, and obtained the results set forth in Table 3. The esters of trichloromethylethylphosphonic acid were likewise synthesized by Rizpolozhensky and kindly placed at our disposal [4].

TABLE 3

No.	Formula	Dipole moment in D
1	$C_2H_5-P(=O)(-OCH_3)-CCl_3$	3.20
2	$C_2H_5-P(=O)(-OC_2H_5)-CCl_3$	3.15
3	$C_2H_5-P(=O)(-OC_3H_7\text{-n})-CCl_3$	3.29
4	$(C_2H_5O)_2-P(=O)-CCl_3$	3.25

As we see from Table 3, the dipole moments of esters of trichloromethylethylphosphonic acid range from 3.15 to 3.29 D and the mean value for the series is 3.21 D.

We calculated the D of molecular models of rigid structures and of models allowing for free rotation of OR groups, assuming the dipole moment of the P → C bond to be 0.8 D, and that of the $P-CCl_3$ bond to be 2.3 D and the direction from phosphorus to chlorine. The dipole moment of the rigid structure A_3 is equal to 3.51 D; that of B_3 is equal to 2.71 D, and differs from the experimentally found value, while the dipole moment of the model with free rotation of the OR groups is 2.33 D.

If the direction of the dipole moment of the $P-C-Cl_3$ bond in the molecule of an ester of trichloromethylethylphosphonic acid is assumed to be from phosphorus to carbon and chlorine, and the dipole moment of the P ← C bond is taken to be equal to 0.8 D, then the dipole moment of the structure A_3 is equal to 3.56 D and that of B_3 is equal to 1.97 D. The dipole moment on the assumption of free rotation of OR groups becomes equal to 3.27 D and nearly equal to the experimentally determined value (Fig. 4.). Consequently, if we assume for an ester of trichloromethylethylphosphonic acid a dipole moment of the $P-C-Cl_3$ bond, direction from phosphorus to carbon and chlorine, of 2.3 D, then the experimentally determined dipole moment (3.21 D) approaches most closely to that calculated on the assumption of a dipole moment of 0.8 D for the P−C bond and a direction from carbon to phosphorus (3.27 D). However, a direction of the dipole moment of the $P-C_2H_5$ bond from carbon to phosphorus is at variance with the general course of shift of electrons in the molecule of an ester of trichloromethylethylphosphonic acid.

On the other hand, the dipole moment of the trichloromethyl radical may be calculated from the dipole moment of chloroform, which is 1.15 D. The dipole moment of CCl_3 is then equal to 0.75 D with a direction from carbon to chlorine, while the dipole moment of the $P-C-Cl_3$ bond is equal to the sum of the dipole moments of the P−C and $C-Cl_3$ bonds and is equal to 1.6 D if the dipole moment of the P−C bond is directed from phosphorus to carbon, and nearly equal to zero if the dipole moment of the P−C bond is directed from carbon to phosphorus.

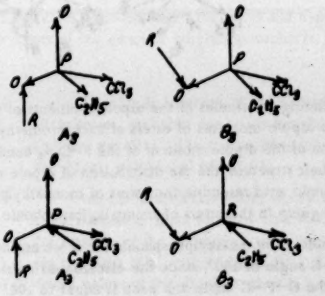


Fig. 4

For determination of the magnitude and direction of the dipole moment of the $P-C-Cl_3$ bond we made use of the dipole moment of diethyl trichloromethylphosphonate. The structure of the molecule of diethyl trichloromethylphosphonate is similar to that of esters of phosphoric acid, only differing in that one OR group is replaced by the trichloromethyl radical, CCl_3. The dipole moment of diethyl trichloromethylphosphonate was measured by us and found to be 3.25 D.

If we assume that the dipole moment of the P–CCl_3 bond is 1.60 D and is directed from phosphorus to carbon and chlorine, then the dipole moment of the molecule of an ester of trichloromethylphosphonic acid with free rotation of the OR groups is 2.55 D, which is less by 0.7 than the experimentally determined value. The experimental value of the dipole moment of diethyl trichloromethylphosphonate (3.25 D) corresponds to that calculated on the assumption of free rotation of the OR groups only in the event that the dipole moment of the P–CCl_3 bond is equal to zero or 4.15 D.

A zero value of the dipole moment of the P–CCl_3 bond could only arise if the dipole moment of the P–C bond was equal to 0.8 D and directed from carbon to phosphorus, and if the dipole moment of the C–Cl_3 bond was 0.8 D and directed from carbon to chlorine. The change of the electronegativity of the P–C bond from 2.1 to 2.5 D and of the C–Cl bond from 2.5 to 3.0 D is nearly identical, and notwithstanding the considerable electron shift, in the P = O bond and in the two P–O bonds, the phosphorus atom is more electronegative than the C atom due to the intense electronic shift in the three C–Cl bonds.

If we assume that the dipole moment of the P ← C → Cl_3 bond is also zero in the molecule of ester of trichloromethylethylphosphonic acid, then the dipole moment determined by experiment (3.21 D) nearly coincides with the value (3.05 D) calculated on the assumption of a pyramidal structure for the molecule of ester of trichloromethylethylphosphonic acid. The dipole moment of the P–C_2H_5 bond is assumed to be equal to 0.8 D and directed from phosphorus to carbon, while the irregular alkoxy group may be able to rotate freely round the P–O bond.

Consideration of the interatomic distances of the molecule of ester of trichloromethylethylphosphonic acid indicates the possibility of free rotation of the OR groups.

EXPERIMENTAL

The dielectric constants and densities of monoesters of ethylphosphonous acid, of esters of ethylphosphonic acid and of esters of trichloromethylphosphonic acid were determined in benzene solutions at 25°. The dipole moments were calculated from the formula :

$$\mu = 0.0127 \cdot 10^{-18} \sqrt{(P_{\infty} - P_{el.} - P_{at.}) \cdot 298},$$

where $P_{el.}$ is the MR and is calculated from the Lorentz-Lorenz formula; P_{at} is equal to 5% of $P_{el.}$. The compounds had the constants set forth in the paper of Arbuzov and Rizpolozhensky [2,4]. The determined values of dielectric constants, densities and polarizations of the benzene solutions of various concentrations of the investigated substances are set forth in Tables 4 to 20.

TABLE 4

$C_2H_5-\underset{\underset{O}{\|}}{\overset{H}{\overset{\diagdown}{P}}}-OCH_3$

c_2	ε_{12}	d_{12}	P_{12}	P_2
0.004159	2.3339	0.8749	27.51	244.2
0.008762	2.3962	0.8764	28.63	232.1
0.01260	2.4533	0.8765	29.22	233.6
0.01554	2.4917	0.8782	29.72	226.0
0.01932	2.5575	0.8786	30.61	233.4
0.02192	2.6020	0.8798	31.17	234.4
0.00000	2.2725	0.8742	26.61	

P_{∞} = 235.00 P_{A+E} = 26.80

P_{or} = 208.20; μ = 3.17 D

TABLE 5

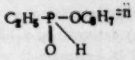
$C_2H_5-\underset{\underset{O}{\|}}{\overset{H}{\overset{\diagdown}{P}}}-OC_2H_5$

c_2	ε_{12}	d_{12}	P_{12}	P_2
0.002004	2.3077	0.8740	27.16	283.7
0.002911	2.3219	0.8743	27.38	276.5
0.004279	2.3456	0.8746	27.72	278.3
0.005486	2.3628	0.8750	27.97	268.0
0.007205	2.3888	0.8752	28.36	264.5
0.008754	2.4125	0.8754	28.70	270.1

P_{∞} = 285.0 ; P_{A+E} = 32.15

P_{op} = 252.85 μ = 3.48 D

TABLE 6

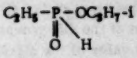


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,003298	2,3217	0,8741	27,39	255,4
0,003991	2,3334	0,8739	27,59	260,9
0,006106	2,3629	0,8749	28,02	251,5
0,008510	2,4033	0,8756	28,30	257,6
0,010150	2,4130	0,8754	28,78	237,8

P_∞ = 274,00; P_{el} = 37,15

P_{or} = 236,85 μ = 3,37 D

TABLE 7

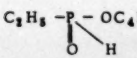


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,002039	2,3032	0,8740	27,10	251,7
0,004723	2,3478	0,8742	27,80	270,7
0,002748	2,3158	0,8739	27,30	267,1
0,005482	2,3586	0,8749	27,94	263,0
0,006085	2,3684	2,8747	28,10	265,8
0,007248	2,3846	0,8750	28,35	261,6

P_∞ = 270,0; P_{el} = 37,10;

P_{or} = 232,90; μ = 3,34 D

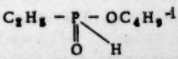
TABLE 8



c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,001572	2,2999	0,8743	27,04	283,1
0,004244	2,3423	0,8745	27,71	279,7
0,002762	2,3178	0,8744	27,34	277,6
0,005079	2,3548	0,8742	27,93	279,6
0,007410	2,3934	0,8749	28,52	278,3
0,006648	2,3840	0,8749	28,36	281,7
0,000	2,2725	0,8734	26,64	

P_∞ = 284,0 P_{A+E} = 41,97; P_{op} =242,00; μ=3,41 D

TABLE 9



c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,002289	2,3051	0,8743	27,15	243,2
0,00300	2,3169	0,8738	27,34	259,1
0,004785	2,3436	0,8745	27,75	258,2
0,005716	2,3559	0,8746	27,95	255,4
0,006073	2,3615	0,8747	28,01	252,1
0,008246	2,3821	0,8755	28,36	235,1

P_∞ = 280,00; P_{A+E} = 42,00

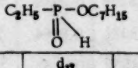
P_{op} = 238,00; μ = 3,38 D

TABLE 10

c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,002581	2,3147	0,8741	27,33	289,1
0,001408	2,2945	0,8736	26,95	282,9
0,002995	2,3215	0,8738	27,44	294,4
0,003828	2,3340	0,8737	27,65	290,1
0,005003	2,3550	0,8743	27,99	295,7
0,006636	2,3822	0,8746	28,41	292,2
0,0000	2,2725	0,8734	26,64	

P_∞= 286,0; P_{A+E} = 51,74; P_{op} =234,26; μ = 3,36 D

TABLE 11

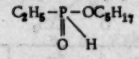


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,001721	2,2986	0,8738	27,07	277,9
0,003648	2,3301	0,8738	27,61	290,4
0,002285	2,3060	0,8738	27,19	286,8
0,004120	2,3365	0,8738	27,72	286,6
0,004665	2,3454	0,8739	27,86	286,7
0,006193	2,3696	0,8739	28,27	290,0

P_∞ = 284,0; P_{A+E} = 56,72

P_{op} = 227,28 μ = 3,33 D

TABLE 12

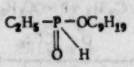


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,001289	2,2938	0,8739	26,99	284,0
0,002151	2,3076	0,8739	27,23	310,0
0,002838	2,3149	0,8739	27,24	287,9
0,003944	2,3324	0,8739	27,59	280,6
0,004650	2,3435	0,8744	27,84	289,1
0,005333	2,3528	0,8744	27,99	284,9

P_{∞} = 284,00; P_{A+E} = 61,62;

P_{or} = 222,38 μ = 3,27 D

TABLE 13

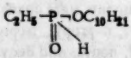


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,002737	2,3093	0,8734	27,29	303,5
0,001477	2,2955	0,8734	27,06	299,0
0,003587	2,3272	0,8734	27,62	295,3
0,004568	2,3417	0,8734	27,87	294,8
0,006518	2,3429	0,8734	28,44	300,4
0,005252	2,3568	0,8734	28,12	308,1
0,0000	2,2725	0,8734	26,64	

P_{∞} = 299,0; P_{A+E} = 66,49;

P_{or} = 232,51; μ = 3,34 D

TABLE 14

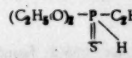


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,002243	2,3077	0,8736	27,17	302,5
0,001192	2,2921	0,8735	26,98	312,1
0,003384	2,3253	0,8735	27,58	305,3
0,003902	2,3308	0,8735	27,70	296,2
0,004411	2,3401	0,8735	27,85	305,7
0,005152	2,3570	0,8735	28,14	316,7

P_{∞} = 315,00; P_{A+E} = 70,00

P_{or} = 243,00; μ = 3,42 D

TABLE 15

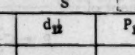


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,002147	2,3099	0,8740	27,24	304,1
0,004343	2,3372	0,8740	27,71	272,9
0,006183	2,3611	0,8750	28,09	260,5
0,007095	2,3769	0,8750	28,35	266,8
0,008473	2,3992	0,8761	28,66	265,9
0,0000	2,2725	0,8732	26,64	

P_{∞} = 273,00; P_{A+E} = 50,00

P_{or} = 223,00; μ = 3,27 D

TABLE 16

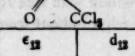


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,001829	2,2938	0,8736	27,04	233,7
0,003598	2,3156	0,8743	27,39	233,5
0,004333	2,3248	0,8740	27,58	241,6
0,005933	2,3461	0,8748	27,95	243,9
0,007539	2,3668	0,8752	28,28	242,6
0,0000	2,2725	0,8732	26,65	

P_{∞} = 242,00 P_{A+E} = 60,69

P_{or} = 181,31 μ = 2,95 D

TABLE 17

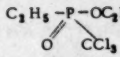


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,002836	2,3121	0,8757	27,31	257,5
0,001297	2,2910	0,8741	26,95	263,0
0,004144	2,3298	0,8770	27,58	250,3
0,005779	2,3543	0,8790	27,95	250,2
0,007616	2,3798	0,8803	28,36	251,8
0,0000	2,2725	0,8731	26,64	

P_{∞} = 261,0; P_{A+E} = 48,22;

P_{or} = 212,78 μ = 3,20 D

TABLE 18

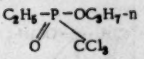


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.003484	2.3241	0.8763	27.50	269.9
0.001403	2.2929	0.8744	26.96	259.6
0.004775	2.3422	0.8773	27.70	247.7
0.005885	2.3588	0.8787	27.98	255.4
0.006608	2.3694	0.8790	28.22	266.5
0.0000	2.2725	0.8732	26.64	

P_{∞} = 260.0; P_{A+E} = 53.41;

P_{or} = 206.59; μ = 3.15 D

TABLE 19

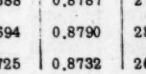


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.001593	2.2966	0.8745	27.07	282.9
0.002839	2.3168	0.8753	27.40	290.6
0.003958	2.3309	0.8769	27.62	271.3
0.004939	2.3490	0.8775	27.91	283.2
0.007142	2.3842	0.8796	28.48	284.0

P_{∞} = 283; P_{A+E} = 57.78

P_{op} = 225.22; μ = 3.29 D

TABLE 20



Mol. wt. 255.5; found MR 50; calculated MR 50.25

c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.001463	2.2931	0.8755	26.97	272.8
0.002965	2.3142	0.8776	27.78	260.5
0.004159	2.3317	0.8785	27.62	270.4
0.005098	2.3465	0.8795	27.83	267.7
0.006071	2.3618	0.8807	28.08	269.2
0.007029	2.3704	0.8814	28.22	257.6
0.0000	2.2725	0.8744	26.64	

P_{∞} = 273.0; P_{A+E} = 52.5;

P_{or} = 220.5; μ = 3.25 D

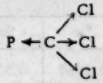
SUMMARY

1. Measurements were made of the dipole moments of the methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, hexyl, heptyl, octyl, nonyl, and decyl esters of ethylphosphorous acid. The mean value of the dipole moment of the series was 3.35 D and it was higher than the mean value for the dialkylphosphorous acids (3.08 D).

2. Measurements were made of the dipole moments of the ethyl and n-propyl esters of ethylthiophosphonic acid (mean value of dipole moment 3.08 D) and of the methyl, ethyl and n-propyl esters of trichloromethylethylphosphonic acid. The mean value for the esters of trichloromethylethylphosphonic acid was 3.21 D.

3. Evaluations were made for all the compounds of the geometrical structure and magnitude and direction of the dipole moments of the individual bonds.

4. Calculations of the dipole moments of esters of trichloromethylethylphosphonic acid for various models lead to the conclusion that the esters have a pyramidal structure with free rotation of the OR groups, with a direction of the dipole moment of the P ⟶ C bond in the ethyl radical from phosphorus to carbon, and a dipole moment of



equal to zero due to compensation of the moments of the P ⟵ C and the C ⟶ Cl_3 bonds.

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[5] B. A. Arbuzov and T. G. Shavsha, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 6, 795.

Received June 19, 1953

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*(T.p. = Consultant's Bureau Translation Pagination)

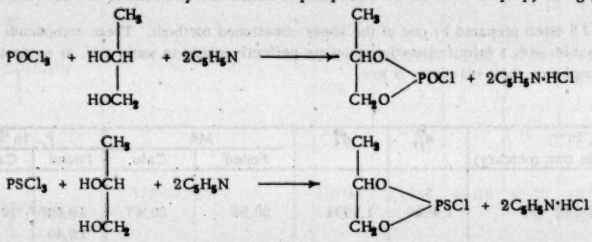
ESTERS OF PROPYLENE GLYCOL PHOSPHORIC AND PROPYLENE GLYCOL THIOPHOSPHORIC ACIDS

B. A. Arbuzov, K. V. Nikonorov and Z. G. Shishova

Cyclic esters of phosphorous acid have recently begun to be studied. Starting in 1945, A. E. Arbuzov and Zoroastrova [1], later in collaboration with Rizpolozhensky [2] and Azanovskaya [3], synthesized and described a series of chlorides and esters of ethylene, propylene, trimethylene and α-chloropropylene glycol phosphorous acids. Esters of glycol phosphoric acids, however, have not previously been studied.

In this communication we present the results of synthesis of cyclic esters of propylene glycol phosphoric and thiophosphoric acids.

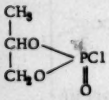
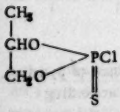
Reaction of phosphorus oxychloride with propylene glycol in presence of hydrogen chloride-binding media yielded the acid chloride of propylene glycol phosphoric acid. Similarly the chloride of propylene glycol thiophosphoric acid was obtained by the action of phosphorus thiochloride on propylene glycol:



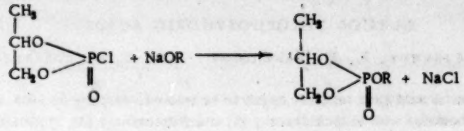
The chlorides of propylene glycol phosphoric and thiophosphoric acids are colorless liquids fuming in the air and resembling the chlorides of dipropylphosphoric and thiophosphoric acids in properties. These compounds are considerably more stable than the corresponding chlorides of phosphorous and thiophosphorous acids. When sealed into glass ampoules they are storable without change for a long period. They react slowly with cold water, but if a base is added to the water they react violently with considerable heat development.

Purification of the chlorides of propylene glycol phosphoric and thiophosphoric acids prepared by the above method was a difficult matter, particularly in respect of the first compound. Vacuum distillation leads to resinification of a considerable proportion of the crude product and the yield of pure acid chloride is low. Further syntheses of cyclic esters of propylene glycol were effected with the undistilled chloride of propylene glycol phosphoric acid.

TABLE 1

Formula	B.p. in °C (p in mm mercury)	d_4^{20}	n_D^{20}	Yield in %	MR Found	MR Calc.
	102-105 (4)	1.4210	1.4520	21	29.31	29.06
	82-84 (3)	1.3902	1.5090	43.5	37.05	37.08

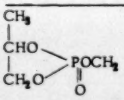
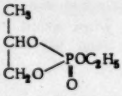
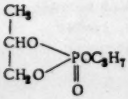
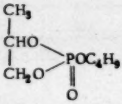
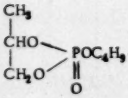
We synthesized the cyclic esters of propylene glycol phosphoric acid by the action of propylene glycol phosphoryl chloride on sodium alkoxides or on alcohols in presence of pyridine according to the following equations:



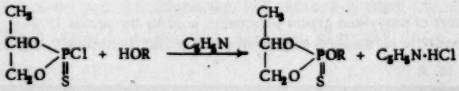
or

In Table 2 are listed 5 esters prepared by one of the above-mentioned methods. These compounds are colorless or light-yellow liquids with a faint fruity odor; they are perfectly stable to water and, as compounds containing pentavalent phosphorus, their reactivity is low.

TABLE 2

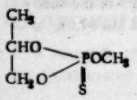
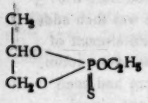
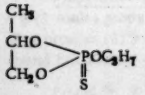
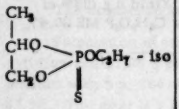
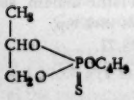
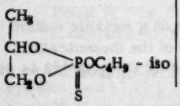
Formula	B.p. in °C (p in mm mercury)	n_D^{20}	d_4^{20}	MR		% P, in %		Yield %
				Found	Calc.	Found	Calc.	
	114-118 (5)	1.4250	1.2734	30.55	30.47	19.92 19.40	20.4	33
	105-108 (3)	1.4265	1.2095	35.17	35.09	18.59 18.50	18.66	34
	116-118 (3)	1.4290	1.1623	39.98	39.71	17.0 16.6	17.2	34
	127-130 (3)	1.4312	1.1211	44.58	44.64	15.1	15.98	32.2
	122-124 (3)	1.4310	1.1331	44.33	44.64	16.0 16.3	15.98	32.2

In a similar way, by the action of propylene glycol thiophosphoryl chloride on alcohols in presence of pyridine, dimethyaniline or diethylaniline, cyclic esters of propylene glycol thiophosphoric acid were obtained according to the equation:



In Table 3 are set forth the constants of 6 esters prepared by this method. These compounds are colorless, highly refractive liquids with a faint odor. Like the oxygenated analogs, they are stable and extremely inert compounds.

TABLE 3

Formula	B.p. in °C (p in mm mercury column)	n_D^{20}	d_4^{20}	MR		P in %		Yield %
				Found	Calc.	Found	Calc.	
	121-123 (11)	1.4828	1.2639	37.98	37.96	18.45 18.55	18.45	41.8
	107-108 (6)	1.4770	1.2086	42.52	42.58	17.25 16.90	17.03	55
	110-112 (5)	1.4741	1.1696	47.09	47.20	16.10 15.90	15.8	61
	104-106 (3)	1.4750	1.1734	46.50	47.20	15.92 16.14	15.8	38
	114-116 (3)	1.4730	1.1435	51.50	51.81	14.72 15.05	14.78	52.4
	112-115 (3)	1.4720	1.1386	51.65	51.81	14.89 14.88	14.78	38

All the compounds that we have described were tested for insecticidal action on the grain weevil and exhibited an action many times weaker than that of tetraethyl pyrophosphate and tetraethyl monothiophosphate.

EXPERIMENTAL

Preparation of propylene glycol phosphoryl chloride. To a mixture of 22.8 g (0.3 mole) propylene glycol, 89.4 g (0.6 mole) diethylaniline and 200 ml dry ethyl ether was added, with stirring at a temperature (in the reaction flask) of −3.0°, 46.05 g (0.3 mole) phosphorus oxychloride in the course of 2 hours. Cooling was then discontinued and the temperature brought to that of the room. This operation took 2.5-3 hours. The resultant diethylaniline hydrochloride was filtered off; the ether was distilled off from the filtrate and the residue distilled in vacuum to give 10 g (21% of the theoretical) of product with b.p. 102-105° (4 mm); d_4^{20} 1.4210; n_D^{20} 1.4520; Found MR 29.31; Calculated for $C_3H_6O_3PCl$ MR 29.06.

Found %: P 19.3, 19.2
Calculated %: P 19.8. $C_5H_6O_3PCl$.

Preparation of propylene glycol thiophosphoryl chloride. Into a three-necked 500 ml flask, equipped with stirrer, dropping funnel and thermometer, were charged phosphorus thiotrichloride, 68 g (0.4 mole), pyridine, 63.5 g (0.8 mole) and 300 ml dry ethyl ether. To the mixture (cooled to -3°) was added 30.5 g (0.4 mole) propylene glycol with continuous stirring over a period of 60 minutes. After the calculated amount of propylene glycol had been added, the reaction mass was gradually heated to 35° and held at this temperature for 2 hours. The pyridine hydrochloride was filtered off (105 g); the ether was driven off and the residue (69 g) distilled in vacuum. Two distillations gave a product with b.p. 82-84 °(3 mm) in amount of 30 g or 43.5% of the theoretical; this was a colorless liquid with a pungent, unpleasant odor; d_4^{20} 1.3902; n_D^{20} 1.5090; found MR 37.05 calculated for $C_3H_6O_2PSCl$ MR 37.08.

Found %: P 18.4; 18.2; Cl 20.7; 20.65.
Calculated %: P 18.0 Cl 20.58. $C_3H_6O_2PSCl$.

Preparation of ethyl propylene glycol phosphate. At the start sodium ethoxide was prepared from 3.67 g sodium and 70 ml ethanol in 100 ml dry ethyl ether; 25 g propylene glycol phosphoryl chloride was then added dropwise with stirring and cooling (temperature in flask 0 to 2°). After addition of the calculated amount of acid chloride, stirring was continued for another 2 hours while the temperature was raised to that of the room. The sodium chloride was separated the next day by centrifuging. After the ethanol-ether mixture had been driven off, the residue was fractionated in vacuum. 9 g (24% of the theoretical) of ethyl propylene glycol phosphate was isolated with the following constants: b.p. 105-108° (3 mm); d_4^{20} 1.208; n_D^{20} 1.4265; found MR 35.90; calculated for $C_5H_{11}O_4P$ MR 35.09.

Found %: P. 18.5; 18.59
Calculated: P 18.66. $C_5H_{11}O_4P$.

Ethyl propylene glycol phosphate is a yellow liquid with a pleasant fruity odor.

Preparation of methyl propylene glycol phosphate. The procedure was similar to the previous one. Reactants were 50 ml methanol, 3.67 g metallic sodium, 25 g propylene glycol phosphoryl chloride. Yield 8 g (33% of product with b.p. 114-118° (5 mm) d_4^{20} 1.273; n_D^{20} 1.4250; found MR 30.55; calculated for $C_4H_9O_4P$ MR 30.47.

Found %: P 19.92; 19.40
Calculated %: P 20.4. $C_4H_9O_4P$.

Methyl propylene glycol phosphate is a yellowish liquid with a fairly pleasant odor.

Preparation of propyl propylene glycol phosphate. Reactants were 80 ml propanol, 3.68 g metallic sodium, and 25 g propylene glycol phosphoryl chloride in 150 ml dry ethyl ether. Yield 10 g (34.8%) of product with b.p. 116 - 118° (3 mm); d_4^{20} 1.1623; n_D^{20} 1.4290; found MR 39.93 calculated for $C_6H_{13}O_4P$ MR 39.71.

Found %: P 17; 16.6.
Calculated %: P 17.2. $C_6H_{13}O_4P$.

Propyl propylene glycol phosphate is a yellowish liquid with a pleasant odor.

Preparation of butyl propylene glycol phosphate. Reactants were 80 ml butyl alcohol, 3.68 g metallic sodium and 25 g propylene glycol phosphoryl chloride in 100 ml dry ethyl ether. Yield 10 g (32.2% of the theoretical) of product with b.p. 127-130° (3 mm); d_4^{20} 1.121; n_D^{20} 1.4312; found MR 44.58; calculated for $C_7H_{15}O_4P$ MR 44.64.

Found %: P 15.5
Calculated %: P 15.98. $C_7H_{15}O_4P$.

Butyl propylene glycol phosphate is a yellowish liquid with a pleasant odor.

Preparation of isobutyl propylene glycol phosphate. Reaction conditions were similar to those previously applied. Materials used were 8.5 g isobutanol, 9.08 g pyridine, 100 ml dry ethyl ether, and 18.2 g propylene glycol phosphoryl chloride. Yield 10 g product (32.2% of the theoretical) with b.p. 122-124° (3 mm); d_4^{20} 1.133; n_D^{20} 1.4310; found MR 44.33; calculated for $C_7H_{15}O_4P$. MR 44.64.

Found %: P 16; 16.3
Calculated %: P 15.98. $C_7H_{15}O_4P$.

Isobutyl propylene glycol phosphate is a light-yellow liquid with a fruity odor.

Preparation of methyl propylene glycol thiophosphate. Into a round-bottomed flask, equipped with stirrer, dropping funnel and thermometer, were charged 60 ml dry ethyl ether, 3.2 g (1 mole) methanol and 7.9 g (1 mole) pyridine. The mixture was cooled to +3° and during 15 minutes 17.2 g (1 mole) propylene glycol thiophosphoryl chloride was added at a liquid temperature of +3 to +10°. After the calculated amount of acid chloride had been added, the contents of the flask were stirred at room temperature for 4 hours. The precipitate of pyridine hydrochloride was then filtered off and the ether was taken off through the water jet pump. The residue was washed several times with water, dried with sodium sulfate and distilled in vacuum. The product had b.p. 121-123° (11 mm); yield 7 g (41.8% of the theoretical; d_4^{20} 1.2639; n_D^{20} 1.4828; found MR 37.98; calculated for $C_4H_9O_3PS$ MR 37.96. Methyl propylene glycol thiophosphate is a colorless liquid with an unpleasant odor.

Found %: P 18.45, 18.55
Calculated %: P 18.45 $C_4H_9O_3PS$

Preparation of ethyl propylene glycol thiophosphate. Operating conditions were as above. From 4.6 g (1 mole) ethyl alcohol, 7.9 g pyridine (1 mole), 17.2 g propylene glycol thiophosphoryl chloride in a medium of dry ethyl ether (70 ml) was obtained 10 g product (55% of the theoretical) with b.p. 107-108°; d_4^{20} 1.209; n_D^{20} 1.4770; found MR 42.52; calculated for $C_5H_{11}O_3PS$ MR 42.58. Ethyl propylene glycol thiophosphate is a colorless liquid with an unpleasant odor.

Found %: P 17.25; 16.9
Calculated %: P 17.03. $C_5H_{11}O_3PS$.

Preparation of propyl propylene glycol thiophosphate. Reaction was carried out with 70 ml dry ethyl ether, 6 g (1 mole) propyl alcohol, 7.9 g (1 mole) pyridine, and 17.2 g (1 mole) propylene glycol thiophosphoryl chloride. 12 g product (61% of the theoretical) was obtained with b.p. 110-112° (5 mm); d_4^{20} 1.187; n_D^{20} 1.4741; found MR 47.09; calculated for $C_6H_{13}O_3PS$ MR 47.20.

Found %: P 16.1, 15.9
Calculated %: P 15.8 $C_6H_{13}O_3PS$.

The compound is a colorless liquid with an unpleasant odor.

Preparation of isopropyl propylene glycol thiophosphate. From 6 g (1 mole) isopropanol, 7.9 (1 mole) pyridine and 17.25 g propylene glycol thiophosphoryl chloride in 70 ml dry ethyl ether was obtained 6.5 g product with b.p. 104-106° (3 mm); d_4^{20} 1.188; n_D^{20} 1.4740; found MR 46.50; calculated for $C_6H_{13}O_3PS$ MR 47.20. The ester is a colorless liquid with an unpleasant odor.

Found %: P 15.92; 16.14.
Calculated %: P 15.8 $C_6H_{13}O_3PS$.

Preparation of butyl propylene glycol thiophosphate. From 7.4 g (1 mole) butanol, 7.9 g (1 mole) pyridine, and 17.25 g (1 mole) propylene glycol thiophosphoryl chloride in 70 ml dry ether was obtained 11 g product (52.4% of the theoretical) with b.p. 114-116° (3 mm); d_4^{20} 1.1435; n_D^{20} 1.4730; found MR 51.50; calculated for $C_7H_{15}O_3PS$ MR 51.81. Butyl propylene glycol thiophsphate is a colorless liquid with an unpleasant odor.

Found %: P 14.72; 15.05
Calculated %: P 14.78. $C_7H_{15}O_3PS$.

Preparation of isobutyl propylene glycol thiophosphate. From 7.4 g (1 mole) isobutanol, 7.9 g (1 mole) pyridine, and 17.25 g (1 mole) propylene glycol thiophosphoryl chloride in 70 ml dry ethyl ether was obtained 8 g (38% of the theoretical) of product with b.p. 112-115° (3 mm); d_4^{20} 1.138; n_D^{20} 1.4720; Found MR 51.65; Calculated for $C_7H_{15}O_3PS$ MR 51.81. The isobutyl ester is a colorless liquid with an unpleasant odor.

Found %: P 14.89; 14.88
Calculated %: P 14.78 $C_7H_{15}O_3PS$.

SUMMARY

1. A study was made of the action of phosphorus oxychloride and phosphorus thiotrichloride on propylene glycol in presence of hydrogen chloride-binding media. The chlorides of propylene glycol phosphoric and propylene glycol thiophosphoric acids were synthesized.

2. 12 new mixed cyclic esters of phosphoric and thiophosphoric acids were synthesized by the action of pro-

pylene glycol phosphoryl and thiophosphoryl chlorides on sodium alkoxides or on alcohols in presence of pyridine.

LITERATURE CITED

[1] A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1952, No. 5, 770. (T.p. 697)*

[2] A. E. Arbuzov, V. M. Zoroastrova, and N. I. Rizpolozhensky, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1948, No. 2, 208.

[3] A. E. Arbuzov and M. M. Azanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1949, No. 5, 473.

Received December 7, 1953

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* T.p. = Consultants Bureau Translation pagination.

THE ACTION OF ALKYL HALIDES ON ESTERS OF ANTIMONOUS AND THIOANTIMONOUS ACIDS

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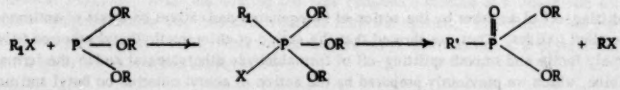
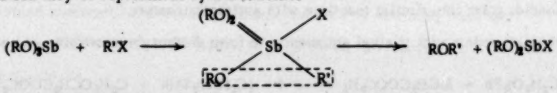
As was shown by A. E. Arbuzov [1], the full esters of phosphorous acid undergo rearrangement under the action of alkyl halides to form esters of alkylphosphonic acids:



Kamai [2] failed to effect the analogous rearrangement of esters of arsenious acid. On acting with alkyl halides upon esters of arsenious acid, he obtained crystalline substances, whose analyses corresponded to products of addition of the alkyl halide to the ester of arsenious acid. Kamai did not investigate these products further.

Experiments on the action of alkyl halides on esters of antimonous acid have not been described. Having engaged in a study of esters of antimonous acid [3], we carried out experiments on the action of alkyl halides on antimonous esters and obtained somewhat unexpected results. The reaction yielded an ether and a dialkoxyhalostibine. The reaction may be represented by the scheme:

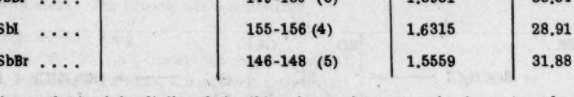


The reaction does not proceed smoothly and is accompanied by the separation of antimony trioxide, metallic antimony, and (in the case of alkyl iodides) iodine. The dialkoxyhalostibines prepared in this way are set forth in the table.

TABLE

$(RO)_2SbX$	M.p. in °C.	B.p. in °C (p in mm mercury)	d_4^{20}	Amount of Sb, in %	
				Found	Calculated
$(C_2H_5O)_2SbI$	72-76	—	—	36,33	35,95
$(C_2H_5O)_2SbBr$	66-67	113-115 (5)	—	42,09	41,73
$(n\text{-}C_4H_9O)_2SbI$		161-163 (10)	1,6481	30,75	30,85
$(n\text{-}C_4H_9O)_2SbBr$		149-150 (6)	1,5931	35,54	35,01
$(i\text{-}C_5H_{11}O)_2SbI$		155-156 (4)	1,6315	28,91	28,79
$(i\text{-}C_5H_{11}O)_2SbBr$		146-148 (5)	1,5559	31,88	32,37

We also synthesized the dialkoxyhalostibines by another route – by the action of acetyl halide on antimonous esters. Kabachnik, Divinsky and Sidorenko [4] showed that in the case of esters of trithiophosphorous acid the action of alkyl halides can proceed differently. The reaction gives chlorides of esters of dithiophosphorous acids, and a thioether is cleaved off. The course of the reaction of Kabachnik and co-workers may be explained by the formation of a sulfonium compound as an intermediate product:



It was interesting to study the reaction of alkyl halides with esters of trithioantimonous acid. Our experiments showed that the reaction of alkyl halides with trithioantimonous esters takes place with considerably greater facility than with antimonous esters, and that it leads to the chloride of the ester of dithioantimonous acid and the

corresponding sulfide:

$$(RS_3)Sb + R'X \longrightarrow (RS)_2SbX + R\overset{\cdot}{-}S-R'.$$

The following compounds were prepared in this way:

$(C_2H_5S)_2SbI$ with b.p. 161-162° (7 mm); d_4^{20} 2.2030

$(C_2H_5S)_2SbBr$ with b.p. 151-152° (8 mm); d_4^{20} 2.1090

Splitting-off of an ether by the action of halogenated derivatives on esters of antimonous acid is not limited to simple alkyl halides. Thus, we showed that the action of chloromethylbutyl ether on tributyl antimonite results in extremely facile and smooth splitting-off of formaldehyde dibutylacetal and in the formation of dibutoxychlorostibine, which we previously prepared by the action of acetyl chloride on butyl antimonite [3].

$$(C_4H_9O)_3Sb + ClCH_2OC_4H_9 \longrightarrow (C_4H_9O)_2SbCl + C_4H_9OCH_2OC_4H_9.$$

This reaction may proceed even further. Thus, the action of butylchloromethyl ether on dibutoxychlorostibine brings about ready detachment of dibutylformal and formation of butoxychlorostibine.

$$(C_4H_9O)_2SbCl + ClCH_2OC_4H_9 \longrightarrow (C_4H_9O)SbCl_2 + C_4H_9OCH_2OC_4H_9.$$

Esters of haloacids enter into similar reactions with antimonous esters.

Ethyl bromoacetate reacts with triethyl antimonite to form diethoxybromostibine and ethyl ethoxyacetate:

$$(C_2H_5O)_3Sb + BrCH_2COOC_2H_5 \longrightarrow (C_2H_5O)_2SbBr + C_2H_5OCH_2COOC_2H_5.$$

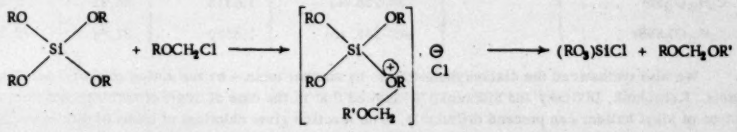
The reaction of esters of antimonous acid with halogenated derivatives may be considered to proceed with intermediate formation of both derivatives of pentavalent antimony

$$(C_2H_5O)_3Sb : + RX = [(C_2H_5O)_3\overset{\oplus}{S}bR]\overset{\ominus}{X},$$

and of compounds of the oxonium type:

$$\left[(C_2H_5O)_2Sb-\underset{R}{\overset{\oplus}{O}}-C_2H_5\right]\overset{\ominus}{X}.$$

It seemed to us that indirect confirmation of the possibility of the reaction proceeding in the second of the above directions might be obtained by experiments on the reaction of α-haloethers on esters of acids other than antimonous acid



Experiment showed, however, that even in very drastic conditions, with prolonged heating at 250-260° of chloromethylmethyl ether with tetraethyl silicate, reaction does not take place. The data obtained speak rather against the oxonium scheme. We must, however, be cautious in drawing a close analogy between orthosilicic esters and esters of antimonous acid. On the other hand, if we accept the scheme for addition of alkyl halide to antimony, the formation of an ether containing a radical of halogenated derivative requires migration of the radical from antimony to oxygen.

All these considerations prompted us to regard the mechanism of the reactions considered in this paper as still unclarified and as requiring further investigations.

EXPERIMENTAL

Preparation of isoamyl antimonite ; Into an Arbuzov flask were put 7 g ethyl antimonite and 7,5 g isoamyl alcohol from fusel oil. At 110-120° the ethanol (b.p. 78-84°) came off in amount of 3,6 g. Distillation in vacuum gave a fraction of 7,2 g with b.p. 150,5-151° (3 mm); d_4^{20} 1,189; n_D^{20} 1,4764.

Found %: Sb 31,54
Calculated %: Sb 31,03. $C_{15}H_{33}O_3Sb$.

Action of methyl iodide on ethyl antimonite. 15 g ethyl antimonite and 8,3 g methyl iodide were heated in a sealed tube for 3 hours at 130-135°. After the heating the tube contents consisted of a liquid and a crystalline product, which was filtered. Slight pressure was detected when the tube was opened. The filtrate was fractionated to give 5,1 g substance with b.p. 95-96° (11 mm). This was unreacted ethyl antimonite. The crystalline product had m.p. 72-76°; yield 8,3 g (61,5% of reacted ethyl ester).

Found %: Sb 36,92; 37,08
Calculated %: Sb 35,95 $C_4H_{10}O_2ISb$.

Action of ethyl iodide on ethyl antimonite. 15 g ethyl antimonite and 9,1 g ethyl iodide were heated in a sealed tube for 2,5 hours at 170-180°. The resultant crystalline product was filtered off and washed with ether. Fractionation of the filtrate gave the fractions:

Fr. I., b.p. 33-40°; 2,3 g (ethyl ether).
Fr. II., b.p. 90-92° (7 mm); 6,1 g (ethyl antimonite).

In the tube remained a deposit of metallic antimony, iodine and antimony trioxide.

The crystalline product has m.p. 71-76°; yield 6,4 g (55,6% on the reacted ethyl antimonite.)

Found %: Sb 36,75; 36,33.
Calculated %: Sb 35,95 $C_4H_{10}O_2ISb$.

Action of ethyl bromide on ethyl antimonite. 15 g ethyl antimonite and 6,4 g ethyl bromide were heated in a sealed tube for 4 hours at 190-195°. The crystalline product resulting from the reaction was filtered off and washed with ether. On the walls of the tube was a deposit of antimony, iodine and antimony trioxide. Fractionation gave:

Fr. I., b.p. 34-40°, 2,1 g (ethyl ether)
Fr. II., b.p. 79-81° (3 mm); 2,8 g (ethyl antimonite)
Fr. III., b.p. 109-111° (3 mm); 2,1 g (crystalline product with m.p. 66-67°; yield 4,7 g, 48% of theoretical).

Found %: Sb 42,09; 42,36.
Calculated %: Sb 41,73. $C_4H_{10}O_2BrSb$.

Action of n-propyl bromide on ethyl antimonite. 15 g ethyl antimonite and 7,2 g n-propyl bromide were heated in a sealed tube for 6 hours at 200-205°. The crystalline product resulting from the reaction was filtered and washed with ether. The filtrate was fractionated.

Fr. I., b.p. 60-63°; 2,4 g
Fr. II., b.p. 70-72°; 1,8 g (unreacted propyl bromide)
Fr. III., b.p. 80-82° (3 mm); 4,6 g (ethyl antimonite)
Fr. IV., b.p. 108-111° (3 mm); 2,6 g; M.p. 65-66°

On the walls of the tube was a deposit of antimony trioxide. Fraction I was redistilled and had b.p. 62-63°; n_D^{20} 1,3739; it was ethylpropyl ether. Literature data [6]: b.p. 63,6°; n_D^{20} 1,36948. Yield of crystalline product 3,3 g ; 29% of the theoretical. Its physical constants correspond to those of diethoxybromostibine obtained by the action of ethyl bromide on triethoxystibine.

Action of methyl iodide on n-butyl antimonite. 15 g n-butyl antimonite and 6,2 g methyl iodide were heated in a sealed tube for 3,6 hours at 185-190°. Fractionation of the reaction product gave:

Fr. I., b.p. 68-72°; 2,9 g
Fr. II., b.p. 138-160° (8 mm); a few drops
Fr. III., b.p. 161-163° (8 mm); 8,2 g; d_4^{20} 1,6841; yield 54%.

A deposit of antimony, iodine, and antimony trioxide remained on the sides of the tube and flask. Fraction I was redistilled and had b.p. 70-71°; n_D^{20} 1,3793; it was methylbutyl ether. Literature data [7]: b.p. 70,3°;

n_D^{20} 1.3720. Fraction III is a reddish liquid.

Found %: Sb 31.21; 30.75
Calculated %: Sb 30.85 $C_8H_{18}O_2ISb$

Action of ethyl bromide on butyl antimonite. 10.5 g n-butyl antimonite and 3.7 g ethyl bromide were heated for 12 hours at 200-210°. Fractionation gave:

Fr. I., b.p. 90-96°; 2.1 g.
Fr. II., b.p. 149-150° (6 mm); 5.2 g; d_4^{20} 1.5931; yield 49.9%.

On the walls of the tube and flask was a deposit of antimony trioxide. Fraction I was redistilled and had b.p. 92-93°; n_D^{20} 1.3705; it was ethylbutyl ether. Literature data [8]: b.p. 91.4°. Fraction II was a viscous liquid, readily hydrolyzing in the air.

Found %: Sb 35.54; 35.78
Calculated %: Sb 35.01. $C_6H_{13}O_2BrSb$.

Action of methyl iodide on isoamyl antimonite. 8 g isoamyl antimonite and 3 g methyl iodide were heated in a sealed tube for 6 hours at 185-200°. The reaction products were fractionally distilled.

Fr. I., b.p. 87-92°; 1.9 g
Fr. II, b.p. 142-150° (4 mm); a few drops
Fr. III., b.p. 155-156° (4 mm); d_4^{20} 1.6315; 3.8 g; yield 43.2%.

On the walls of the tube and flask was a deposit of iodine, antimony and antimony trioxide. Fraction I was redistilled and had b.p. 90-91°; n_D^{20} 1.3895; it was methylisoamyl ether. Literature data [9]: b.p. 91°. Fraction III was a reddish liquid, easily hydrolyzed in the air.

Found %: Sb. 28.91; 28.61.
Calculated %: Sb 28.79 $C_{10}H_{22}O_2ISb$.

Action of ethyl bromide on isoamyl antimonite. 11 g isoamyl antimonite and 3.2 g ethyl bromide were heated in a sealed tube for 9 hours at 185-210°. The reaction products were fractionally distilled:

Fr. I. b.p. 109-112°; 2.8 g
Fr. II., b.p. 146-148° (5 mm); d_4^{20} 1.5559; 4.5 g; yield 42%.

On the walls of the tube and the flask was a deposit of antimony trioxide. Fraction I was redistilled and had b.p. 111-112°; n_D^{20} 1.3923; it was ethylisoamyl ether. Literature data [10]: b.p. 112°. Fraction II was a viscous liquid, easily hydrolyzed in the air.

Found %: Sb 31.88, 31.79
Calculated %: Sb 32.37 $C_{10}H_{22}O_2BrSb$.

Action of hexyl chloride on ethyl antimonite. 7.5 g ethyl antimonite and 3.4 g n-hexyl chloride were heated in a sealed tube for 8 hours at 200-215° and even at 250°. No reaction took place between these compounds.

Action of methyl iodide on ethyl trithioantimonite. 10 g ethyl trithioantimonite and 4.8 g methyl iodide were heated for 2.5 hours at 80-85°. The reaction products were fractionally distilled:

Fr. I., b.p. 67-70°; 2.1 g
Fr. II., b.p. 144-165° (9 mm); 0.6 g
Fr. III ., b.p. 162-163° (8 mm); d_4^{20} 2.2030; 3.2 g; yield 26.4 %.

On the walls of the tube and the flask was a deposit of antimony, sulfur and iodine. Fraction I was redistilled and had b.p. 66-68°; n_D^{20} 1.4410; it was methylthioethyl ether. Literature data [11]: b.p. 66.5-67.5°. Fraction III was a reddish liquid with an unpleasant odor; easily hydrolyzed in the air.

Found %: Sb 32.51; 33.14
Calculated %: Sb 32.85 $C_4H_{10}S_2ISb$.

Action of ethyl iodide on ethyl trithioantimonite. 10 g ethyl trithioantimonite and 6.1 g ethyl iodide were heated in a sealed tube at 75-80° for 1.5 hours. The products of reaction were fractionally distilled:

Fr. I., b.p. 90-94°; 3.3 g

Fr. II., b.p. 151-160° (7 mm); 0.6 g
Fr. III., b.p. 161-162° (7 mm); d_4^{20} 2.2028; 5.6 g; yield 46.0%

On the walls of the tube and flask was a deposit of sulfur, iodine and antimony. Fraction I was redistilled and had b.p. 92-93°; n_D^{20} 1.4476; it was ethyl sulfide. Literature data [12]: b.p. 92.2-93°; n_D^{20} 1.4423. Fraction III was the iodoanhydride of ethyl dithioantimonite.

Action of ethyl bromide on ethyl trithioantimonite. 10.5 g ethyl trithioantimonite and 3.9 g ethyl bromide were heated in a sealed tube for 3 hours at 70-75°. The products of reaction were fractionally distilled:

Fr. I., b.p. 90-94°, 2.8 g
Fr. II., b.p. 151-152° (8 mm); d_4^{20} 2.1090; 5.2 g; yield 46.8%.

Fraction I was redistilled and had b.p. 92-93°; n_D^{20} 1.4452; it was diethyl thioether. Fraction II was a yellowish liquid with an unpleasant odor, easily hydrolyzed in the air.

Found %: Sb 38.22; 38.24
Calculated %: Sb 37.61 $C_4H_{10}S_2BrSb$.

Action of chloromethylbutyl ether on butyl antimonite. To 9 g butyl antimonite in an Arbuzov flask was slowly added 3.2 g chloromethylbutyl ether; heat was developed. The reaction products were fractionally distilled:

Fr. I., b.p. 65-70° (11 mm); 3.9 g
Fr. II., b.p. 148-149° (11 mm); d_4^{20} 1.5073; 6.5 g; yield 82%

Fraction I was redistilled and had b.p. 67° (11 mm); d_4^{20} 0.8362; n_D^{20} 1.4075; it was formaldehyde dibutylacetal. Literature data [13]: b.p. 180.5-181°; d_4^{20} 0.8366; n_D^{20} 1.4072. Fraction II was dibutoxychlorostibine. Literature data [3]: b.p. 150-151° (13 mm);

Action of chloromethylbutyl ether on chlorodibutoxystibine. Into a Claisen flask was charged 5.2 g dibutoxychlorostibine, and 2.1 g chloromethylbutyl ether was slowly added; heat was liberated. The whole of the reaction mass crystallized on standing. The reaction products were fractionally distilled:

Fr. I., b.p. 66-69° (11 mm); 2.4 g
Fr. II., b.p. 124-126°; M.p. 84-85°; 3.9 g; yield 86%

Fraction I was redistilled and had b.p. 67° (11 mm); n_D^{20} 1.4076; d_4^{20} 0.8360; it was formaldehyde dibutylacetal. Fraction II was dichlorobutoxystibine. Literature data [3]: b.p. 125-126° (11 mm); M.p. 83-85°.

Action of ethyl bromoacetate on ethyl antimonite. 10 g ethyl antimonite and 6.5 g ethyl bromoacetate were heated in a sealed tube for 12 hours at 160-170°. A crystalline substance came out on standing. The reaction products were subjected to fractionation:

Fr. I., b.p. 50-62° (12 mm)
Fr. II., b.p. 95-98° (12 mm); 2.1 g (ethyl antimonite)
Fr. III., b.p. 125-126° (12 mm); M.p. 67-69°; 6.2 g; yield 66.6%.

Fraction I was redistilled and had b.p. 52-54° (12 mm); d_4^{20} 0.9780; n_D^{20} 1.4092. Literature data [14]: b.p. 158° (752 mm); d_4^{25} 0.9754. Fraction III was bromodiethoxystibine.

Action of chloromethylmethyl ether on ethylorthosilicate. 15 g ethyl orthosilicate and 5.8 g chloromethylmethyl ether were heated in a sealed tube for 36 hours at 250-260°. On fractionation the original substances were recovered unchanged. A part of the chloromethylmethyl ether decomposed.

SUMMARY

1. Alkyl halides react with esters of antimonous acid with cleavage of ethers and formation of dialkoxyhalostibines. In this way the preparation was effected of diethoxy-, dibutoxy-, diisoamyloxybromostibines and of diethoxy-, dibutoxy- and diisoamyloxyiodostibines.

2. Reaction of alkylchloromethyl ethers with antimonous esters leads to separation of the corresponding formals and to formation of alkoxychlorostibines.

$$(RO)_3Sb + CH_2Cl - OR' \longrightarrow (RO)_2SbCl + ROCH_2OR'$$

$$(RO)_2SbCl + CH_2Cl - OR' \longrightarrow (RO)SbCl_2 + ROCH_2OR'$$

3. Alkyl halides readily react with esters of trithioantimonous acid to form dialkyl sulfide and the haloanhydrides of dithioantimonites. The bromoanhydride of diethyl dithioantimonite and the corresponding iodoanhydride were prepared.

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Received June 19, 1953

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ANOMALOUS REACTIONS OF SODIUM DIETHYL PHOSPHITE AND OF TRIETHYL PHOSPHITE WITH SOME HALOGENATED DERIVATIVES

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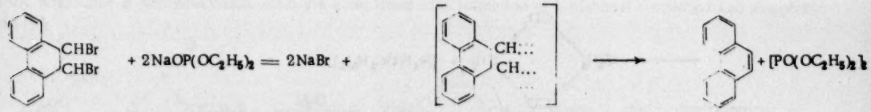
In 1929 A. E. Arbuzov and B. A. Arbuzov [1] observed a difference in the course of the reaction of sodium diethyl phosphite with triphenylmethyl chloride and bromide. With triphenylmethyl chloride the normal reaction product is formed – the ester of triphenylmethylphosphoric acid, whereas with triphenylmethyl bromide the free triphenylmethyl radical is formed.

Later we [2] showed that diphenylchloromethane and diphenylbromomethane behave similarly with sodium diethyl phosphite. With the chloride the ester of diphenylmethylphosphonic acid is formed; with the bromide, tetraphenylethane is formed. With a benzyl halide this difference in the behavior of halogen derivatives disappears, and reaction with the chloride, bromide and iodide gives the ester of benzylphosphonic acid. The reactions of dimerization of radicals during the action of sodium diethyl phosphite on halogenated derivatives has also been observed in other cases. A. E. Arbuzov and V. S. Abramov [3] found that in the action of sodium diethyl phosphite on bromoethyl malonate, ethanetetracarboxylic acid ester is formed. Shavan [4] showed that dimerization of radicals proceeds in the reaction of sodium diethyl phosphite with esters of halosubstituted acids.

We studied the reactions of sodium diethyl phosphite and triethyl phosphite with various types of halogen derivatives with the aim of making a close study of the anomalous course of the reaction with sodium diethyl phosphite, and thereby of establishing the causes of this behavior of sodium diethyl phosphite and the halogen derivative during double exchange reactions. As the experiments showed, dinaphthylchloromethane, dinapthylbromomethane, 9-chlorofluorene and 9-bromofluorene do not react with sodium diethyl phosphite even when heated to 140°. Interesting results were obtained with 9,10-dibromophenanthrene and sodium diethyl phosphite in an ethereal medium; phenanthrene was isolated in 90% yield. A similar picture was obtained in the reaction of dibromophenanthrene with triethyl phosphite. Here again phenanthrene was isolated in a yield of over 90%. The phosphorus-containing products of the reaction were not examined in detail. Fractions with constants similar to those of diethylphosphoric acid were isolated.

The following mechanism may be advanced for these reactions: sodium diethyl phosphite and triethyl phosphite function as bromine acceptors; a diradical is formed which is stabilized by formation of phenanthrene.

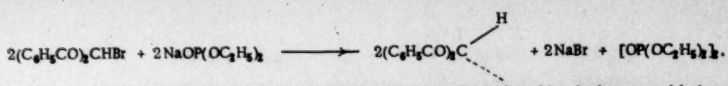


The reaction of the dibromo compound proceeds in like manner to the reaction of tetramethylethylene dibromide with sodium diethyl phosphite, which leads to tetramethylethylene [2].

Diethyl phosphorous acid could have been formed by hydrolysis of the ester. Formation of diethyl phosphorous acid in the reaction with triethyl phosphite is still unclarified.

We obtained entirely unexpected results on reacting sodium diethyl phosphite or triethyl phosphite with dibenzoylbromomethane and tribenzoylbromomethane. The main products of reaction were respectively dibenzoylmethane and tribenzoylmethane. Distillation of the phosphorus-containing portion of the reaction products in both cases gave a product whose constants and analysis corresponded to triethyl phosphate.

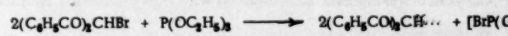
The mechanism of this oxidation-reduction reaction cannot be considered to be clarified. In the present stage of the investigation a radical scheme for the reaction seemed to us most probable:



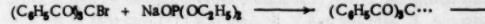
The resultant dibenzoylmethyl radical reacts with the solvent (ether), detaching hydrogen and being reduced to dibenzoylmethane. An alternative route to dibenzoylmethane involved disproportionation of dibenzoylmethyl. In that event, however, tetrabenzoylethylene should be formed, and no trace of the latter could be detected.

Formation of the ethyl phosphate is puzzling. It may be mentioned that when chlorine acts upon sodium diethyl phosphite, the products include triethyl phosphate [5].

Formation of dibenzoylmethane in the reaction with the bromo compound takes place without a solvent. The reaction may be represented by the equation:

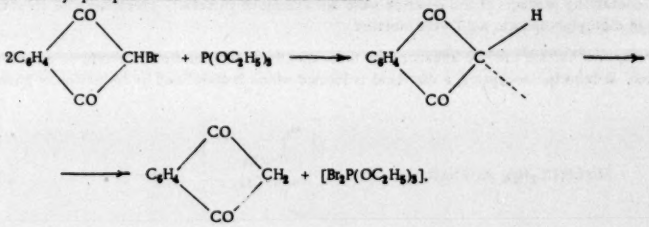


In this case the reduction of dibenzoylmethyl must be considered to take place at the expense of the hydrogens of triethyl phosphite. A similar reaction course was observed in the interaction of sodium diethyl phosphite or of triethyl phosphite with tribenzoylbromomethane:

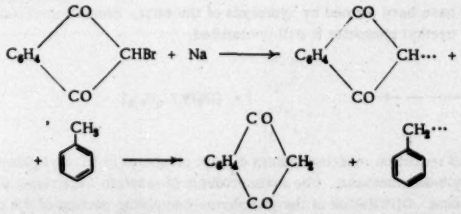


In this case again, the reduction must evidently proceed at the expense of the solvent (ether). Triethyl phosphate was isolated in addition to tribenzoylmethane. With the aim of confirming the suggested reaction scheme, we carried out experiments on the action of metallic sodium upon dibenzoylbromomethane and tribenzoylbromomethane in a toluene medium. The reaction does not take place smoothly, although in the first case dibenzoylmethane and tetrabenzoylethylene were isolated, and in the second case tribenzoylmethane, thus providing indirect confirmation of the proposed scheme, since the dibenzoylmethane and tribenzoylmethane must have been formed from the respective radicals of dibenzoylmethyl and tribenzoylmethyl.

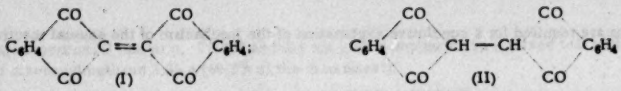
The results obtained prompted us to undertake the reaction of sodium diethyl phosphite and of triethyl phosphite with other halogenated derivatives containing two carbonyl groups in the α-position to the carbon linked with the halogen. We selected for this purpose bromoindandione and its derivatives. Bromoindandione reacts smoothly with triethyl phosphite and is reduced to indandione:



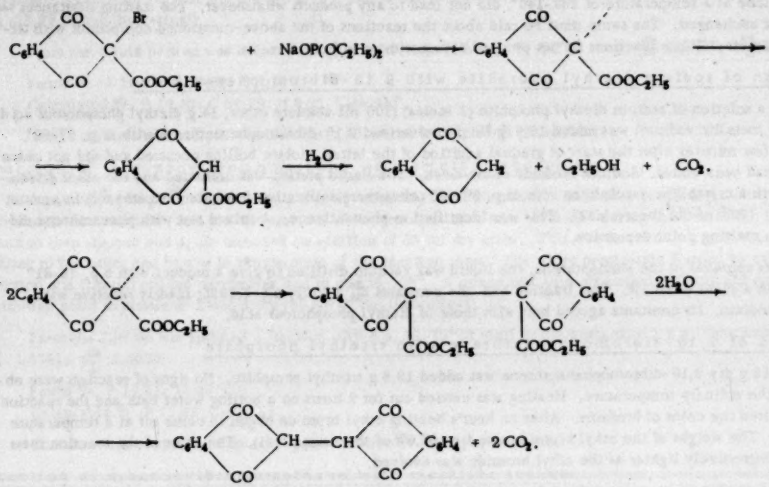
This reaction course is confirmed by the action of metallic sodium on bromoindandione in a toluene medium which leads to indandione:



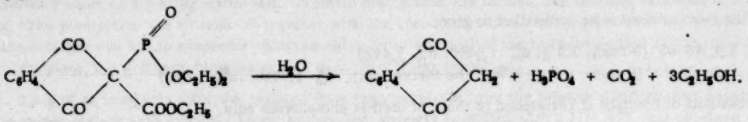
The reaction between bromoindandione and sodium diethyl phosphite is more complicated. Diphthalylethene (I) and diphthalylethane (II) are evidently formed.



We have investigated the action of sodium diethyl phosphite and triethyl phosphite on ethyl bromoindandionecarboxylate. Indandione and diphthalylethane were isolated. In the present stage of the investigation the most probable explanation of this reaction course involves the formation of the free radical of the ester of indandionecarboxylic acid and the dimerization of the radical; alternatively reaction might take place with hydrogen donors (in this case the ester) followed by saponification of the ester and cleavage of carbon dioxide from the free acid:

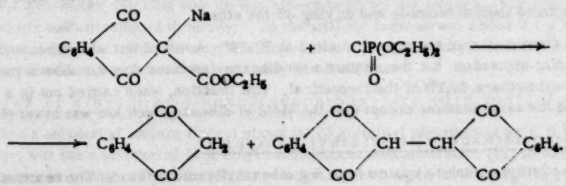


The possibility is not excluded, however, of formation of indandione as a result of saponification of the phosphoric ester since β-ketophosphonic acids are hydrolyzed with formation of a carbonyl compound and phosphoric acid [6]:



With triethyl phosphite, ethyl bromoindandionecarboxylate forms indandione.

It is interesting to note, as our experiments showed, that when the sodium salt of ethyl indandionecarboxylate reacts with diethylphosphorous acid chloroanhydride, indandione and diphthalylethane are formed:



Additional investigations are required for a conclusive explanation of the mechanism of the unusual reactions which we have described.

EXPERIMENTAL

Reaction of dinaphthylchlorobromomethanes and of 9-bromo- and 9-chlorofluorines with sodium diethyl phosphite and with triethyl phosphite

Attempts to effect the reactions between dinaphthylchloro- and bromomethanes and 9-chloro- and 9-bromofluorines and sodium diethyl phosphite in a medium of dry ether, benzene and dioxane, even in some cases in a sealed tube at a temperature of 130-140°, did not lead to any products whatsoever. The starting substances were recovered unchanged. The same must be said about the reactions of the above-mentioned compounds with triethyl phosphite. These reactions do not proceed either with or without solvents.

Reaction of sodium diethyl phosphite with 9,10-dibromophenanthrene

To a solution of sodium diethyl phosphite (2 moles) (100 ml absolute ether, 14 g diethyl phosphorous acid and 2,3 g metallic sodium) was added 15,7 g finely pulverized 9,10-dibromophenanthrene with m.p. 97-98°. Within a few minutes after the start of gradual addition of the latter, violent boiling occurred and did not cease until all had been added. Sodium bromide came down. The liquid portion was collected and the ether driven off to leave a crystalline precipitate with m.p. 92-93° (after recrystallization from absolute ethanol) in amount of 7,3 g (90% of the theoretical). This was identified as phenanthrene. A mixed test with phenanthrene did not give a melting point depression.

After removal of the phenanthrene, the liquid was vacuum distilled to give a product with b.p. 79-81° (12 mm) in a yield of 63,1%. This fraction had the constants d_{20}^{20} 1,0779; n_D^{20} 1,4095; readily reactive with metallic sodium. Its constants agreed best with those of diethyl phosphorous acid.

Reaction of 9,10-dibromophenanthrene with triethyl phosphite

To 19 g dry 9,10-dibromophenanthrene was added 18,6 g triethyl phosphite. No signs of reaction were observed at the ordinary temperature. Heating was carried out for 2 hours on a boiling water bath and the reaction mass acquired the color of bromine. After an hour's heating ethyl bromide began to come off at a temperature of 38-40°. The weight of the ethyl bromide was 4 g (66,6% of the theoretical). The color of the reaction mass became progressively lighter as the ethyl bromide was evolved.

Fractionation in vacuum yielded three fractions. The last fraction, which came over at 176° (5 mm), rapidly crystallized. The crystals had m.p. 97-98° and did not give a depression in admixture with phenanthrene. Yield 8,85 g (98,33% of the theoretical). The identity of the product was confirmed by formation of the picrate which melted at 145° in agreement with the literature.

The first two fractions were redistilled to give:

Fr. I., b.p. 48-63° (8 mm); 2,2 g; d_{20}^{20} 1,0400; n_D^{20} 1,4120
Fr. II., b.p. 63-65° (8 mm); 5,6 g (72% of the theoretical); d_{20}^{20} 1,0740; n_D^{20} 1,4107

The constants of Fraction II correspond to those of diethyl phosphorous acid.

Reaction of sodium diethyl phosphite with dibenzoylbromomethane

A solution of 9 g dibenzoylbromomethane [7] in 10 ml dry benzene was run into sodium diethyl phosphite (75 ml dry ether, 4,2 g diethyl phosphorous acid and 0,68 g metallic sodium). Slight heat was developed during the reaction, and the reaction mass was afterwards heated for 2 hours on a water bath. White crystals were isolated after filtering off the precipitated sodium bromide and driving off the ether.

After two recrystallizations from methanol the crystals melted at 77-78°. A mixed test with dibenzoylbromomethane shows a melting point depression, but the mixture with dibenzoylmethane does not show a melting point depression. Yield of dibenzoylmethane 69,1% of the theoretical. This reaction, when carried out in a medium of dry benzene, presented the same features except that the yield of dibenzoylmethane was lower (42,7%).

Reaction of dibenzoylbromomethane with triethyl phosphite

Dropwise addition of 4,75 g triethyl phosphite was made to 8 g dibenzoylbromomethane. The reaction was violent and the temperature inside the flask rose to 80°. The white crystalline precipitate was separated from the

liquid portion; it had m.p. 77-78° and did not give a depression in a mixed test with debenzoylmethane. Yield of dibenzoylmethane 3.65 g (60.8% of the theoretical).

Reaction of sodium diethyl phosphite with tribenzoylbromomethane

A solution of sodium diethyl phosphite, prepared from 4.3 g diethyl phosphorous acid, 0.72 g metallic sodium and 75 ml dry ether, was run into 11.8 g dry, pulverized tribenzoylbromomethane [8], m.p. 114-115°. On running in the solution of sodium diethyl phosphite, an intense yellow coloration was developed and the temperature of the reaction mass rose to an extent sufficient to boil the ether. After the addition was completed, the reaction mass was heated for 2 hours on a water bath. A voluminous white precipitate was formed which melted at 226-228° after recrystallization from ethanol and did not give a depression in a mixed melting test with tribenzoylmethane. Yield 7 g (58.3% of the theoretical).

From the liquid portion was isolated 1.8 g of a fraction with b.p. 90-91° (8 mm); d_{20}^{20} 1.0766; n_D^{20} 1.4101.

Found %: P 16.97; C 39.64; H 8.18
Calculated %: P 17.03; C 39.59; H 8.22 $C_6H_{15}O_3P$.

In its constants and analysis the fraction is identical with triethyl phosphite [9].

Reaction of tribenzoylbromomethane with triethyl phosphite

4 g triethyl phosphite was run into 8.8 g dry tribenzoylbromomethane. Each drop reacted violently with the tribenzoylbromomethane, and the temperature of the reaction mass rose to 70-80° during the addition. The reaction then stopped and again restarted on addition of 50 ml dry ether. This was marked by commencement of boiling of the ether and by rise in temperature of the reaction mass. The white precipitate formed by the reaction was filtered off and purified; it had m.p. 226-228°. A mixed test with dibenzoylmethane did not give a melting point depression. Yield 3.6 g (56.6% of the theoretical).

From the filtrate was isolated a fraction with b.p. 78-79° (3 mm) in the amount of 1.2 g; constants d_{20}^{20} 1.0741; n_D^{20} 1.4070.

Found %: P 16.51; 16.29
Calculated %: P 17.03 $C_6H_{15}O_3P$.

The constants of this fraction correspond to those of triethyl phosphate.

Reaction of dibenzoylbromomethane with metallic sodium

2.4 g (3 moles) metallic sodium was placed in 70 ml dry toluene, and by very vigorous shaking while the toluene was heated sufficiently to melt the sodium, the latter was converted into a powder. Into the flask was then run 10 g dry dibenzoylbromomethane. Bubbles at once came off fairly energetically. The mixture was heated for 6 hours on a boiling water bath. A white precipitate was formed, the solution darkened to a brown color. The precipitate was filtered off together with the unreacted sodium and washed with dry toluene. The toluene solution was left to evaporate spontaneously; after removal of the resinous portion of the residue on a porcelain plate, 0.5 g dibenzoylmethane with m.p. 76-77° was separated.

2.5 g of an inorganic solid was isolated from the precipitate from the toluene solution after decomposition of the excess sodium with ethanol. From the solution, strongly acidified with 0.1 N HCl, was obtained a yellow precipitate which after recrystallization from ethanol melted at 180-183°, in agreement with the melting point in the literature [10] for tetrabenzoylethylene. Yield 0.3 g.

Reaction of tribenzoylbromomethane with metallic sodium

0.4 g (2 moles) metallic sodium was placed in 25 ml dry toluene. The toluene was heated to the boil and the metallic sodium reduced to powder. To the still hot toluene was added 3.4 g tribenzoylbromomethane. The reaction proceeded as with dibenzoylbromomethane. 2.4 g tribenzoylbromomethane was recovered unchanged. Tribenzoylmethane was isolated in extremely small amount.

Reaction of ethyl bromoindandionecarboxylate with sodium diethyl phosphite

Into a solution of sodium diethyl phosphite (5 g diethyl phosphorous acid, 0.8 g metallic sodium and 50 ml dry ether) was run a solution of 10 g ethyl bromoindandionecarboxylate [11] in absolute ether. A flocculent precipitate came down. The color of the reaction mass changed from orange to yellow, at times becoming dark-green. Heat was liberated during the reaction and the ether boiled. After the reaction mass had been

heated on a water bath for an hour, the yellow precipitate was separated, washed with ether and recrystallized from water: it then melted at above 215° with decomposition. According to the literature [12] it is identical with diphthalylethane. Yield 6.8 g.

From the filtrate at 112-115° (9-10 mm) was distilled off a liquid which soon crystallized to white, well-formed crystals with m.p. 132-134°; weight 2 g. A mixed test of these crystals with indandione did not give a melting point depression. A second experiment gave exactly the same results.

Reaction of ethyl bromoindandionecarboxylate with triethyl phosphite

4 g triethyl phosphite was added dropwise to 6 g dry ethyl bromoindandione carboxylate. The reaction was very violent: the temperature inside the flask rose to 85° and a reddish-brown liquid was formed. The reaction was conducted without supplementary heating. On standing white, acicular crystals came down with m.p. 130-132°. The melting point of a mixed sample with the product from the preceding experiments was 130-131°. Yield 4.9 g.

Reaction of the sodium salt of ethyl indandione carboxylate with diethyl phosphorous acid chloroanhydride

8 g diethyl phosphorous acid chloroanhydride was added dropwise to 10 g sodium salt of ethyl indandione carboxylate. The reaction was conducted with heating to the boiling point of the ester. The reaction mass was diluted with 30 ml dry ether and left overnight. The yellow precipitate was separated by dilution of the reaction mass with ethanol and purified; it melted at 215° with decomposition. Diphthalylethane was isolated; yield 7.5 g. The ethanolic filtrate was worked up to give acicular crystals with m.p. 134°. A mixed test of these crystals with indandione did not give a melting point depression.

Reaction of bromoindandione with sodium diethyl phosphite

To an ethereal solution of sodium diethyl phosphite, prepared from 3.5 g diethylphosphorous acid, 0.53 g metallic sodium and 50 ml dry ether, was added 5 g bromoindandione [11]. The reaction was vigorous and caused the ether to boil. No heat was applied. A precipitate came down which was insoluble in ether but partly soluble in ethanol. The ether-insoluble portion was gray-green in color and weighed 1 g; m.p. 370°. On the basis of the literature data [12], it may be assumed to be the sodium salt of diphthalylethane.

Evaporation of the ethereal filtrate left a black resin which after drying on a porous plate separated 0.35 g of red solid with m.p. 320-322° (with decomp.). On the basis of the same literature data [12] it may be regarded as diphthalylethene.

Reaction of bromoindandione with triethyl phosphite

1.5 g triethyl phosphite without a solvent was run into 1 g bromoindandione. The reaction was performed with rise of temperature to the boiling point of triethyl phosphite. The reaction mass changed into a dark-brown liquid which was heated for 2 hours on an oil bath. After 24 hours crystals had been deposited — small white needles with a yellowish tinge. After recrystallization from alcohol-ether mixture they melted at 130-132°. A mixed test with indandione did not give a depression of melting point. Yield 0.5 g (75.7% of the theoretical). The composition of the isolated compound was confirmed by analysis.

Found %: C 73.36; 73.42; H 4.35; 4.35

Calculated %: C 73.56; H 4.11 $C_9H_6O_2$.

Reaction of bromoindandione with metallic sodium

2.5 g sodium (3 moles) was put into 50 ml dry toluene. The sodium was converted to powder in the boiling toluene. To the mixture of hot toluene and sodium powder was added 6 g bromoindandione. After heating on a water bath, bubbles began to come off. After 1.5 hours' heating on an electric hot plate at the boiling point of toluene, sodium bromide started to come down. The toluene solution was separated from the precipitate and the unreacted sodium. The sodium was dissolved by ethanol. The total weight of sodium bromide and sodium ethoxide was 5.15 g.

From the toluene solution was separated 3.7 g (95% of the theoretical) yellowish powder; after washing with water and thorough drying, it melted at 129-130°. A mixed test with synthetic indandione did not give a depression.

SUMMARY

1. Dinaphthylchloromethane, dinaphthylbromomethane, 9-chlorofluorine and 9-bromofluorine did not

react in the experimental conditions.

2. Phenanthrene was formed by reaction of sodium diethyl phosphite and triethyl phosphite with 9,10-dibromophenanthrene.

3. Dibenzoylbromomethane and tribenzoylbromomethane react with sodium diethyl phosphite or with triethyl phosphite with formation of dibenzoylmethane and tribenzoylmethane.

4. Bromoindandione and the ethyl ester of bromoindandionecarboxylic acid react with sodium diethyl phosphite or with triethyl phosphite with formation of indandione or of products of dimerization of the free indandionyl radical.

5. The most probable reaction scheme, which explains the anomalous course of the bromo compounds with sodium diethyl phosphite or triethyl phosphate, is one involving the assumption of formation of free radicals as intermediate products.

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Received June 19, 1953

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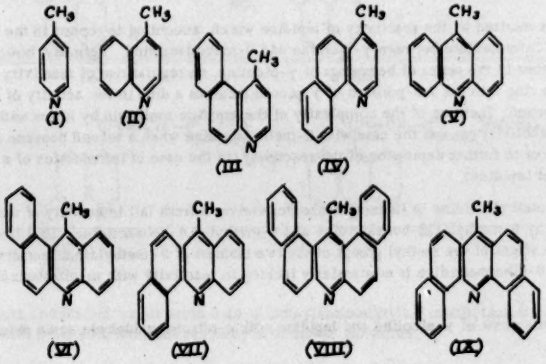
THE RELATIVE REACTIVITY OF THE METHYL GROUPS OF BENZO DERIVATIVES OF 4-METHYLPYRIDINE

B. M. Mikhailov and G. S. Ter-Sarkisyan

The methyl groups of nitrogen-containing heterocyclic compounds located in the α- or γ-position to the nitrogen possess, as we know, labile hydrogen atoms. This lability is manifested by the ability of such compounds to enter into reaction with aldehydes, ketones, aromatic nitroso compounds, diazo compounds, etc. The reactions with aldehydes proceed the most readily, while only few compounds are capable of coupling with diazo compounds.

Porai-Koshits and co-workers [1,2] showed that 9-methylacridine readily reacts with nitroso and diazo compounds, whereas α-and γ-picolines, quinaldine and lepidine [3] enter into these reactions only in the form of quaternary salts. Results of a study of the activity of methyl groups of benzo derivatives of 9-methylacridine, published previously by Porai-Koshits and one of us [4,5], show that the introduction of one, and in still greater measure, two angular condensed benzene rings into the molecule of 9-methylacridine lowers the reactivity of the methyl groups in reactions with aromatic aldehydes, nitrosodimethylaniline and diazo compounds.

In view of the high chemical activity of 9-methylacridine, it seemed of interest to throw more light on the influence of the number and position of the benzene rings upon the reactivity of methyl groups in six-membered nitrogen-containing heterocycles. Compounds of the quinoline series were included in the investigation. We studied the relative activity of the methyl groups of the following compounds: 4-methylpyridine (I), 4-methylquinoline (II), 4-methyl-5,6-benzoquinoline (III), 4-methyl-7,8-benzoquinoline (IV), 9-methylacridine (V), 9-methyl-1,2-benzacridine (VI), 9-methyl-3,4-benzacridine (VII), 9-methyl-1,2,7,8-dibenzacridine (VIII) and 9-methyl-3,4,5,6-dibenzacridine (IX). Their condensations with m-nitrobenzaldehyde were studied.



Condensation of the heterocyclic compounds with m-nitrobenzaldehyde was conducted with heating of equimolar amounts of the starting substances in presence of acetic anhydride in sealed tubes at 150-153° for 1.5 hours. The reactions resulted in formation of the corresponding styryl derivatives.

Due to the low mobility of the hydrogen atoms of the methyl groups of some of the investigated compounds, it was more convenient to evaluate the amount of reacted heterocycle not from the yield of styryl derivative but from the amount of unreacted m-nitrobenzaldehyde. The latter was separated from the heterocyclic compound by treatment of the reaction mass with hydrochloric acid followed by precipitation as the semicarbazone.

In addition the unreacted starting heterocyclic compound was extracted from the acidic solutions, and in some cases also the reaction product.

No great accuracy is claimed for our procedure for determination of the activity of the methyl groups of benzo derivatives of 4-methylpyridine; it only makes possible a relative evaluation of their reactivity. The results obtained are set forth in the table.

TABLE

Heterocyclic compound *	Amount of unreacted m-nitrobenzaldehyde, calculated as semicarbazone %	Observations
4-Methylpyridine	47,85	45% 4-(m-nitrostyryl)-pyridine isolated
4-Methylquinoline	79,8	14% 4-(m-nitrostyryl)-quinoline isolated
4-Methyl-5,6-benzoquinoline	94,0	
4-Methyl-7,8-benzoquinoline	92,11	
9-Methylacridine	43,74	Approximately 47% 9-(m-nitrostyryl)-acridine isolated
9-Methyl-1,2-benzacridine	80,39	
9-Methyl-3,4-benzacridine	76,10	
9-Methyl-1,2,7,8-dibenzacridine	88,82	
9-Methyl-3,4,5,6-dibenzacridine	94,10	Approximately 95% unreacted 9-methyl-3,4,5,6-dibenzacridine isolated

* The weight of sample of heterocyclic compound varied between 0,25 and 0,78 g; the weight of m-nitrobenzaldehyde in all cases was 0,4 g; the amount of acetic anhydride was 5 ml. The melting point of m-nitrobenzaldehyde semicarbazone was in the range of 226-231°.

The experimental data show that the most active of the compounds concerned in the reaction with m-nitrobenzaldehyde is 9-methylacridine; it is closely followed by γ-picoline. All the remaining compounds are considerably less reactive.

Special attention is merited by the reactivity of lepidine which, according to reports in the literature, should have occupied a position intermediate between γ-picoline and 9-methylacridine. Actually, however, in passing from one member to another in the series of benzologs of γ-picoline, no regular rise of reactivity is observed. The introduction of a benzene ring into the 2,3-position of γ-picoline causes a drop in the activity of the methyl groups of the heterocyclic compound. Increase of the complexity of the lepidine molecule by fusion with one benzene ring leads either to a rise of reactivity (as was the case with 9-methylacridine when a second benzene ring was fused to the heterocyclic nucleus) or to further depression of the reactivity (in the case of introduction of a benzene ring in the 5,6- or 7,8-position of lepidine).

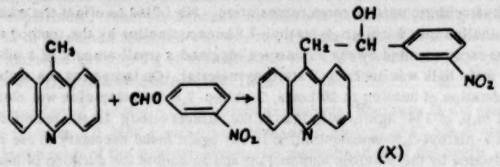
On passing from 9-methylacridine to its monobenzo derivative, a fresh fall in activity of the methyl group is observed, as exemplified by 9-methyl-1,2-benzacridine and 9-methyl-3,4-benzacridine. Still lower mobility is possessed by the hydrogen atoms of the methyl groups of the two isomers of 9-methyldibenzacridine which we investigated: 9-methyl-3,4,5,6-dibenzacridine is substantially lacking in reactivity with m-nitrobenzaldehyde in the specified conditions.

Comparison of the reactions of γ-picoline and lepidine with o-nitrobenzaldehyde again revealed the greater reactivity of the picoline.

At the same time we studied the photochemical reactions of benzo derivatives of lepidine and of 9-methyl acridine with m-nitrobenzaldehyde. On carrying out the reactions of these compounds under the influence of ultraviolet rays, we expected the methylated heterocyclic compounds, due to their greater reactivity, to be more easily amenable to photochemical transformations than the corresponding aromatic hydrocarbons which are known to react with carbonyl compounds under the action of light. This process is usually accompanied by dehydrocondensation of the aromatic hydrocarbons or by a reaction of the type of the aldol condensation [6, 7].

We carried out the photochemical reactions by irradiating benzene solutions of equimolar amounts of m-nitrobenzaldehyde and 4-methylquinoline, 4-methyl-5,6-benzoquinoline, 9-methylacridine, and 9-methyl-1,2-

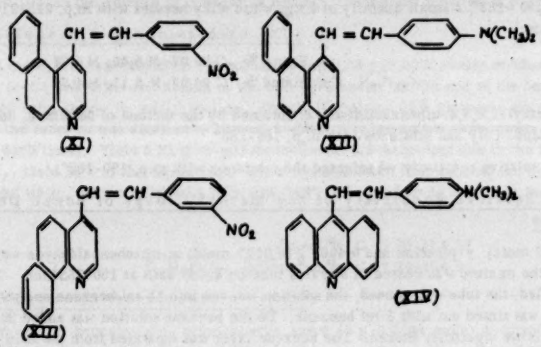
benzacridine with a PRK-2 lamp in a nitrogen atmosphere. The most active of the investigated compounds in photocondensations was again 9-methylacridine. The reaction between 9-methylacridine and m-nitrobenzaldehyde under the action of light is of the aldol condensation type with formation of α-(m-nitrophenyl)-β-(9-acridyl)-ethanol, the yield of which after 100 hours' irradiation was 54 % of the theoretical.



(X)

The remaining compounds do not react with m-nitrobenzaldehyde when irradiated with the mercury lamp for 100 hours. Nevertheless, in spite of the high reactivity of 9-methylacridine, we did not succeed in effecting its condensation with acetone, acetophenone, or benzophenone when exposed to the rays from the quartz mercury lamp. In these cases up to 90 % of the original 9-methylacridine was recovered after irradiation of the mixture under ultraviolet rays for 150 - 180 hours.

In the quaternary salts of methylated heterocycles the methyl group is known to be considerably more active than in the free bases. Due to the low reactivity of the methyl groups of benzo derivatives of lepidine when used in the form of the free bases for the preparation of their styryl derivatives, we made use of the corresponding hydrochlorides. Thus, on heating 5,6-benzolepidine hydrochloride with m-nitrobenzaldehyde and p-dimethylaminobenzaldehyde in acetic anhydride, m-nitrobenzylidene-5,6-benzolepidine (XI) and p-dimethylaminobenzylidene-5,6-benzolepidine (XII) were obtained. Similarly we prepared m-nitrobenzylidene-7,8-benzolepidine (XIII):



In addition to these compounds we prepared 9-(p-dimethylaminostyryl)-2-methylacridine (XIV) by heating 2,9-dimethylacridine with p-dimethylaminobenzaldehyde in acetic anhydride.

EXPERIMENTAL

Starting Substances

Lepidine (II) was prepared by Mikhailov's method [8]. 9-Methylacridine (V) was prepared by the method of Porai-Koshits and Vernikovskaya [9]. After purification via the tartrate [10] it had m.p. 117.5°.

4-Methyl-5,6-benzoquinoline (III) was prepared by the method of Hamilton and Benson [11]; its hydrochloride was obtained by passing dry hydrogen chloride into a benzene solution of 4-methyl-5,6-benzoquinoline; it formed needles with m.p. 224-227°.

9-Methyl-1,2-benzacridine (VI), 9-methyl-3,4-benzacridine (VII) and 9-methyl-3,4,5,6-dibenzacridine (IX) were obtained by the previously described method [5, 6].

4-Methyl-7,8-benzoquinoline (IV) was previously obtained by Hamilton and Gobeil but we introduced some changes in the method. 2-Hydroxy-4-methyl-7,8-benzoquinoline was prepared by 15 minutes' heating of aceto-aceto-1-naphthylamide with concentrated sulfuric acid in a yield of 95.7%. Gibson [12] carried out this cyclization with the help of hydrochloric acid at room temperature. We failed to effect the transformation of 2-hydroxy-4-methyl-7,8-benzoquinoline into 2-chloro-4-methyl-7,8-benzoquinoline by the method of Hamilton and Gobeil [13]. In the conditions recommended by the authors we obtained a small amount of a substance with a wide melting range (130-200°); the main bulk was unchanged starting material. On increasing the amount of chlorinating agents 2.5 times and the duration of heating to 20 hours, 2-chloro-7,8-benzolepidine was obtained in a yield of 64.6% of the theoretical (the m.p. of 134° agrees with that of the authors cited). In the reduction of 2-chloro-4-methyl-7,8-benzoquinoline to 4-methyl-7,8-benzoquinoline it was again found necessary to use more tin and hydrochloric acid than was recommended by the previous authors [13] and to double the duration of heating of the mixture.

9-Methyl-1,2,7,8-dibenzacridine was prepared from β,β-dinaphthylamine which was obtained by Cook's method [14], by heating 2-naphthol with 2-naphthylamine in presence of naphthalene-2-sulfonic acid, in a yield of 80%; m.p. 173-174°. 50 g (0.19 mole) β,β-dinaphthylamine, 20 g (0.19 mole) acetic anhydride and 26 g anhydrous zinc chloride were heated for 5 hours at 185-190° (thermometer in the mixture). The reflux condenser was then put in the sloping position and the temperature raised to 250° to distil off the acetic acid. The mass was then heated for 30 minutes at 250-260°. The resultant dark, viscous resin was repeatedly treated with 10% sulfuric acid.

Neutralization of the acidic solution with 25% ammonia gave 25.5 g dark-yellow substance with m.p. 155-165°. Yield of crude product 46.8% of the theoretical. The precipitate was twice crystallized from benzene, then from ethyl acetate and then twice from ethanol. In this way yellow needles were obtained with m.p. 180-183°.

Found %: C 89.88; H 5.40; N 4.96
$C_{22}N_{15}N$. Calculated %: C 90.07; H 5.11; N 4.79

Chromatographic treatment of the precipitate with m.p. 155-165° on alumina gave, apart from the yellow substance with m.p. 180-183°, a small quantity of long, white silky needles with m.p. 215-216° with the following elementary composition:

Found %: C 90.02; H 5.40; N 4.81
$C_{22}H_{15}N$. Calculated %: C 90.07; H 5.11; N 4.79

Previously 9-methyl-1,2,7,8-dibenzacridine was obtained by the method of Bernthsen, and the author [15] points out that he obtained only one substance with m.p. 184-185°.

For study of the relative reactivity we selected the substance with m.p. 180-183°.

Investigation of Relative Reactivity of the Methyl Groups of Benzo Derivatives of 4-methylacridine

0.2471 g (0.0027 mole) γ-picoline and 0.4000 g (0.0027 mole) m-nitrobenzaldehyde were dissolved in 5 ml acetic anhydride and the mixture was heated in a sealed tube on an oil bath at 150-153° for ~1.5 hours. After the reaction mass had cooled, the tube was opened, the solution was run into 15 ml benzene and transferred to a separating funnel; the tube was rinsed out with 5 ml benzene. To the benzene solution was added 30 ml of 6 N hydrochloric acid and themixture vigorously shaken. The benzene layer was separated from the acid layer and the latter was again treated with 15 ml benzene.

The benzene extracts were combined, washed with water and dried over calcium chloride. The benzene was driven off in vacuum. The residual m-nitrobenzaldehyde in the flask was dried in a vacuum desiccator to constant weight. Yield 0.2188 g or 54.7% of unreacted m-nitrobenzaldehyde. The precipitate of aldehyde was dissolved in the same flask with 2 ml ethanol and to the ethanol solution was added a solution of 0.3 g semicarbazide hydrochloride in 1 ml water. The precipitate of m-nitrobenzaldehyde semicarbazone was filtered off, washed with a few drops of dilute ethanol and dried to constant weight at 100°. Yield 0.2625 g m-nitrobenzaldehyde semicarbazone with m.p. 225-230°, equivalent to 0.1906 g, or 47.85%, of unreacted aldehyde.

Excess of 25% ammonia was added to the acid layer. The resultant voluminous amorphous precipitate was drained, washed with water, and dried at 100° to constant weight. Yield 0.3 g substance (48.2% of the theoretical) with m.p. 139-142°. According to the literature 4-(m-nitrostyryl)-pyridine melts at 144° [16].

In the case of lepidine and acridine derivatives, shaking of a benzene solution with acid brought down a salt. The acidic solution and the precipitate were separated from the benzene solution and again shaken with 15 ml benzene; the precipitate was then filtered through a glass filter. The benzene and aqueous solutions in the filtrate were separated and further working-up was on the same lines as in the case of γ-picoline.

On condensation of γ-picoline with o-nitrobenzaldehyde the reaction mass was worked up in the same conditions as in the preceding experiment. From the benzene solution was obtained 0.1990 g unreacted o-nitrobenzaldehyde, 0.1742 g, or 43.7% of unreacted aldehyde was recovered in the form of its semicarbazone. Neutralization of the acidic layer with ammonia gave 0.29 g of substance (47% of the theoretical) with m.p. 95-101°. According to the literature 4-(o-nitrostyryl)-pyridine melts at 105° [16].

In the case of condensation of lepidine with o-nitrobenzaldehyde, operation in the same conditions led to separation from the benzene solution of 0.3657 g unreacted aldehyde; 0.3500 g, or 57.5% of unreacted o-nitrobenzaldehyde was obtained in the form of the semicarbazone. On neutralization of the acidic solution with excess of 25% ammonia, 0.455 g, or 6.2%, o-nitrobenzylidenelepidine was obtained with m.p. 161-165°. According to the literature the m.p. is 172-173° [17].

Condensation of 9-Methylacridine with m-Nitrobenzaldehyde under the Action of Ultraviolet Rays

1.34 g (0.007 mole) 9-methylacridine and 1.05 g (0.007 mole) m-nitrobenzaldehyde were dissolved in 14 ml benzene (thiophene-free) in a molybdenum glass flask. The air above the liquid was displaced by nitrogen. The solution was irradiated with a PRK-2 lamp for 100 hours. At the conclusion of this period 1.3 g reaction product with m.p. 130-134° was filtered off from the solution. After two crystallizations from benzene and then from dioxane, the substance was obtained in the form of fine, yellow needles with m.p. 146.5-147.5°.

Found %: N 8.10

$C_{21}H_{16}O_2N$. Calculated %: N 8.14

This compound was previously prepared by Sharp and co-workers [19] by heating 9-methylacridine with m-nitrobenzaldehyde at 100° in the absence of condensing agents. The authors reported m.p. 145° [19].

m-Nitrobenzylidene-5,6-benzolepidine (XI)

0.5 g (0.0022 mole) 5,6-benzolepidine hydrochloride and 0.33 g (0.0022 mole) m-nitrobenzaldehyde were dissolved in 1.5 ml acetic anhydride and heated at the boil for 3 hours. At the end of the heating the color of the solution had changed from yellow to reddish-yellow. Water (10 ml) and 25% ammonia were added to the cooled reaction mass until the reaction was alkaline to litmus; a white, oily precipitate came down. This was twice washed with ethanol (3 ml each time). Yield 0.21 g m-nitrobenzylidene-5,6-benzolepidine in the form of yellowish needles with m.p. 144-149°. Yield 30% of the theoretical. After crystallization from ethanol the m-nitrobenzylidene-5,6-benzolepidine formed white, silky needles with m.p. 168-169°. The product is soluble in the common organic solvents.

Found %: C 77.20; H 4.57

$C_{21}H_{14}O_2N_2$. Calculated %: C 77.29; H 4.32

m-Nitrobenzylidene-7,8-benzolepidine (XIII)

1 g (0.0044 mole) 7,8-benzolepidine hydrochloride and 0.65 g (0.0044 mole) m-nitrobenzaldehyde were dissolved in 5 ml acetic anhydride and the mixture boiled for 3 hours. After cooling, the solution was run into 5 ml water; a yellow oil formed and crystallized after a short time. The precipitate was washed 3 times with a small amount of methanol at room temperature (0.31 g, yield 21.8% of the theoretical). After three recrystallizations from methanol and then from ethanol, m-nitrobenzylidene-7,8-benzolepidine formed fine, white needles with m.p. 155-157°. The compound is readily soluble in the common organic solvents.

Found: %: N 9.06

$C_{21}H_{14}O_2N_2$. Calculated %: N 8.68

p-Dimethylaminobenzylidene-5,6-benzolepidine (II)

1 g (0.0044 mole) 5,6-benzolepidine hydrochloride and 0.65 g (0.0044 mole) p-dimethylaminobenzaldehyde were dissolved in 3 ml acetic anhydride and the mixture boiled for 2 hours. At the end of the heating the color of the solution had become cherry-red. After addition of 10 ml water and 5 ml 25% ammonia to the reaction mass,

a red, amorphous precipitate came down. This was filtered off, washed with water and dissolved wet in 5 ml ethanol. The product was reprecipitated from the ethanol solution by addition of 8 ml 20% sodium hydroxide. The orange precipitate was recrystallized from 20 ml ethanol to give 0,38 g (26,9% of the theoretical) of yellow needles. After two crystallizations from ethanol, p-dimethylaminobenzylidene-5,6-benzolepidine formed lemon-yellow needles with m.p. 170,5-171,5°.

Found %: N 9,06

$C_{21}H_{14}O_2N_2$. Calculated %: N 8,68

9-(p-Dimethylaminostyryl)-2-methylacridine (XIV)

2,9-Dimethylacridine was prepared by the method of Bonna [18]. 0,32 g (0,0015 mole) 2,9-dimethylacridine and 0,23 g (0,0015 mole) p-dimethylaminobenzaldehyde were dissolved in 2 ml acetic anhydride and heated for an hour at the boil. At the end of the heating the color of the solution had become dark-brown. After cooling, 0,18 g orange precipitate with m.p. 210-217° was filtered off from the solution. From the mother liquor after neutralization with ammonia was separated a further 0,3 g substance with m.p. approximately 204°. Yield of unpurified product 94% of the theoretical. After crystallization from methanol and then from a mixture of benzene and ligroine, 9-(p-dimethylaminostyryl)-2-methylacridine formed elongated orange rhombs with m.p. 225-226°. The compound dissolves readily in alcohols and benzene.

Found %: N 8,41

$C_{24}H_{22}N_2$. Calculated %: N 8,28

SUMMARY

1. An investigation was made of the lability of the hydrogen atoms of the methyl groups of 4-methylpyridine (I), 4-methylquinoline (II), 4-methyl-5,6-benzoquinoline (III), 4-methyl-7,8-benzoquinoline (IV), 9-methylacridine (V), 9-methyl-1,2-benzacridine (VI), 9-methyl-3,4-benzacridine (VII), 9-methyl-1,2,7,8-dibenzacridine (VIII) and 9-methyl-3,4,5,6-dibenzacridine(IX) in condensation reactions with m-nitrobenzaldehyde. A study was made of the photochemical reactions of the above compounds with carbonyl compounds.

2. It was found that in the condensations of the above compounds with m-nitrobenzaldehyde the activity of the methyl groups falls off on the one hand in the order: (I), >(II), >(III), ≥(IV), and on the other hand in the order: (V), > (VII), ≥ (VI), > (VIII), > (IX).

3. It was shown that, contrary to previously recorded views, the introduction of a benzene ring into the 4-methylpyridine molecule leads to a decline in the reactivity of the methyl group in condensation with o- and m-nitrobenzaldehydes.

4. It was established that the most active of the investigated compounds toward m-nitrobenzaldehyde is 9-methylacridine. Passage from 9-methylacridine to its angular monobenzo derivatives (9-methyl-1,2- and 9-methyl-3,4-benzacridine) is accompanied by a fall in the reactivity of the methyl group. The activity of the methyl group is depressed to a still greater extent in the reaction of m-nitrobenzaldehyde with the angular dibenzo derivatives of 9-methylacridine.

5. It was established that the activity of the methyl group of benzo derivatives of 4-methylpyridine depends not only on the number of benzene rings but also on their position relative to the heterocyclic nucleus. This is particularly marked in the increased reactivity of 9-methylacridine and the low reactivity of the 5,6- and 7,8-benzo derivatives of 4-methylquinoline.

6. The great reactivity of 9-methylacridine in comparison with 5,6- and 7,8-benzo derivatives of lepidine is confirmed by the results of photocondensations of these compounds with m-nitrobenzaldehyde.

7. Several new styryl derivatives of the quinoline series were synthesized.

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Received June 24, 1953

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COMMUNICATION 2. SPECTRAL INVESTIGATIONS OF ALCOHOLIC SOLUTIONS OF CHLORO DERIVATIVES OF ANILINE

A. A. Kharkharov

In spite of the great industrial importance of halogenated aniline derivatives, their ultraviolet spectra have been relatively little studied. It is known that the introduction of a chlorine atom into aniline in the ortho-position to the amino group has little influence upon the field of absorption. The maxima of the main bands of p-chloroaniline and of 2,4-dichloroaniline [1] are appreciably shifted in the direction of long waves in comparison with the maxima of o-chloroaniline and aniline [2 - 10]. We decided to make a systematic study of the spectra of alcoholic solutions of mono-, di-, tri- and tetrachloro derivatives of aniline with the aim of establishing a possible influence of the accumulation of substitutents upon the form of the spectral curve and the position of the maxima.

Our investigations have shown that the spectra of all the chloro derivatives of aniline in the wave-length region of 210 to 800 mμ consist of two principal adjacent absorption bands. The intensity of the short-wave band is greater than that of the long-wave band. Due to the short-wave bands being relatively little altered both by accumulation of substituents and by change in the position of substituents, we limited ourselves to a comparison of the maxima of the long-wave bands.

For monochloro derivatives of aniline (Fig. 1, Table 1) the long-wave maxima are distributed in the sequence:

para > ortho > meta

This proves that the cause of the bathochromic displacements must be sought not only in the inductive influence of the halogen but also mainly in the possibility of development of fields of conjugation. Since the halogen in the para- position to the amino group is separated from the amino group by the longest conjugated chain of carbon atoms, its bathochromic action is the most intense. The halogen in the ortho- position has a considerably weaker effect. In view of the fact that the substitutents in the meta- position are not conjugated with one another, the repulsion of electrons of the amino group by the chlorophenyl residue will be least in this case.

EXPERIMENTAL

The spectral investigations were carried out with the SF-1 photoelectric spectrophotometer in the range of 210 to 700 mμ. The solvent was 96% ethanol. A solvent effect was excluded. All the substances were thoroughly purified (recrystallization from various solvents to constant melting point or distillation in vacuum). Identical concentrations of substances were used throughout.

On passing from monohalogenated to dihalogenated derivatives of aniline, further shifts of the absorption bands are observed in the long-wave direction (Figs. 1,2,3 and Table 1). Of the three dichloro derivatives of aniline that we investigated (1,2,5-; 1,3,4-; 1,2,4-) the greatest bathochromic displacement of the main absorption band occurs with the 1,2,4-isomer (Fig. 2, Table 1). The two other isomers have the same absorption maximum (Table 1, Figs. 2 and 3).

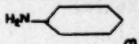
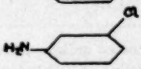
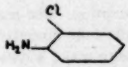
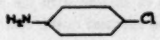
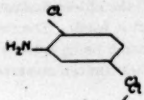
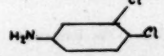
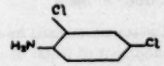
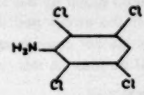
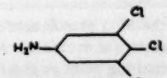
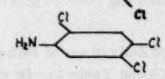
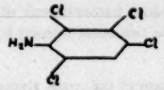
A further bathocromic displacement of the maximum of the main absorption band occurs on introduction into the aniline molecule of three and four atoms of chlorine (Figs. 4 and 5, Table 1), but their absorption likewise does not extend outside the ultraviolet region. 2,4,5-Trichloroaniline (λ_{max} 313 mμ) has a maximum at a longer wave length than 3,4,5-trichloroaniline (λ_{max} 310 mμ). Of the two tetrachloro derivatives that we investigated, 2,3,4,6-tetrachloroaniline has a higher value of absorption maximum than 2,3,5,6-tetrachloroaniline (Fig. 6, Table 1).

In the order of increase of magnitude of the absorption maxima, the chlorinated anilines follow a definite sequence (see formulas on page 740).

A study of the additivity of the effect of substituents seemed to us of considerable theoretical interest. With this objective we compared the observed results for shifting of the main absorption band of di- and higher-substituted anilines with the results calculated by addition of the respective displacements of monohalosubstutited anilines (Table 1, Figs. 3 to 7). It was found that there is a relatively slight deviation from additivity in the case of halogenated derivatives of aniline. The biggest deviation from additivity (− 5 mμ) characterizes 2,4-dichloroaniline (Table 1)

TABLE 1

Main Absorption Maxima of Alcoholic Solutions of Chloro Derivatives of Aniline

No.	Amine	Formula of amine	Main absorption band, in mμ	Shift of maximum, in mμ		Deviation in mμ
				Found	Calculated	
1	Aniline		285	–	–	–
2	m-Chloroaniline		288	3	–	–
3	o-Chloroaniline		293	8	–	–
4	p-Chloroaniline		300	15	–	–
5	2,5-Dichloroaniline		300	15	11	4
6	3,4-Dichloroaniline		300	15	18	–3
7	2,4-Dichloroaniline		303	18	23	–5
8	2,3,5,6-Tetrachloroaniline		308	23	22	1
9	3,4,5-Trichloroaniline		310	25	21	4
10	2,4,5-Trichloroaniline		313	28	26	2
11	2,3,4,6-Tetrachloroaniline		317	32	34	–2

Deviations of a similar order of magnitude are found for 3,4- and 2,5-dichloroanilines (–3 and 4 mμ), also for 2,3,4,6- and 2,3,5,6-tetrachloroanilines (–2 and 1 mμ), but the deviations are respectively of opposite sign). In the case of the trichloroderivatives the greatest observed deviation of the main absorption maximum from the calculated value occurs with the 3,4,5-isomer (Table 1, Figs. 1 to 7).

SUMMARY

1. Absorption spectra of alcoholic solutions of mono-, di-, tri- and tetrachloroanilines were investigated.

2. It was shown that there is a regular shift of the maximum of the main absorption band in the direction of longer wave lengths with increasing number of substituents.

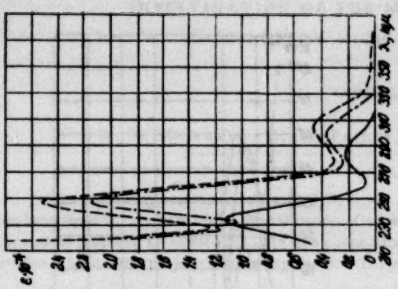


Fig. 3. Absorption spectra of alcoholic solutions of: – aniline; – – 2,4-dichloroaniline; – · – 3,4-dichloroaniline

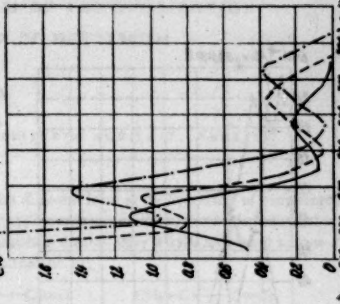


Fig. 4. Absorption spectra of alcoholic solutions of: – aniline; – – 2,5-dichloroaniline; – · – 2,4,5-trichloroaniline

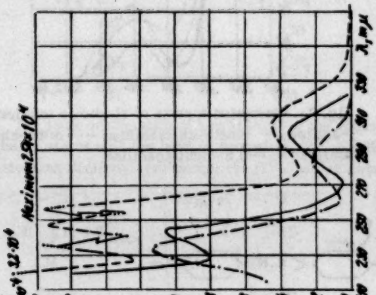


Fig. 2. Absorption spectra of alcoholic solutions of: – 2,5-dichloroaniline; – – 2,4-dichloroaniline; – · – aniline

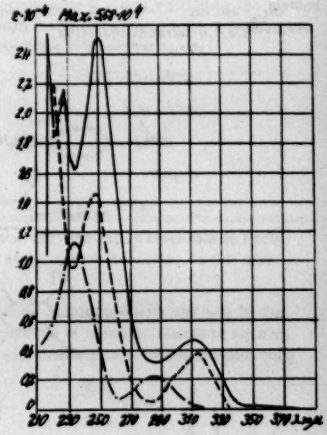


Fig. 5. Absorption spectra of alcoholic solutions of: – – 2,4,5-trichloroaniline, – 3,4,5-trichloroaniline, – · – aniline

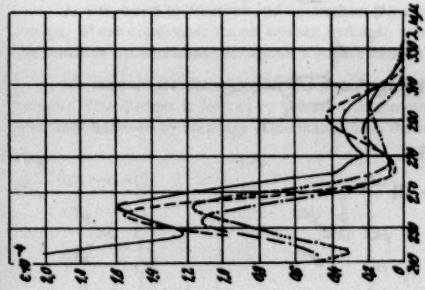


Fig. 1. Absorption spectra of alcoholic solutions of: – – ortho-chloroaniline; – meta-chloroaniline; – · – aniline; – · · – para-chloroaniline

3. It was established that chlorine atoms bring about a relatively small deviation from the addivity of the effect of the substituent. The magnitude of this deviation depends upon the number and position of the substituents.

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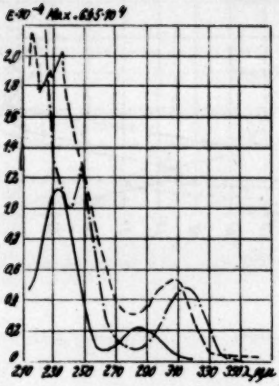


Fig. 6. Absorption spectra of alcoholic solutions of: –aniline; – –2,3,5,6-tetrachloroaniline; –·–2,3,4,6-tetrachloroaniline.

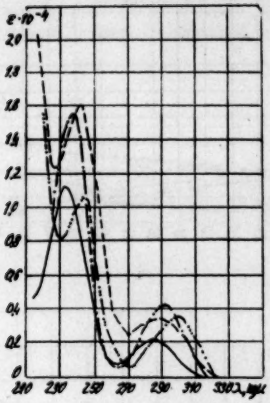
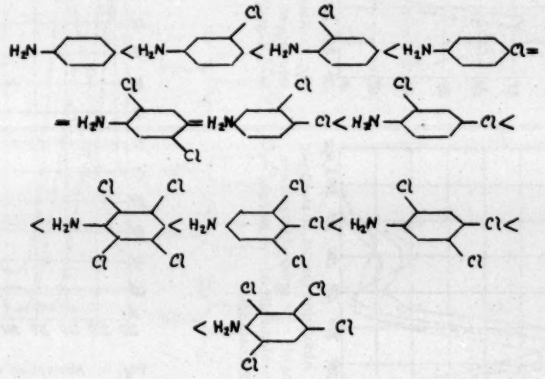


Fig. 7. Absorption spectra of alcoholic solutions of: –aniline; – –meta-chloraniline; –·–ortho-chloroaniline; –···–2,5-dichloroaniline.



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Received November 26, 1953

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INVESTIGATION OF THE MECHANISM OF THE CYCLIZATION REACTION WITH THE HELP OF DEUTERIUM

COMMUNICATION 3

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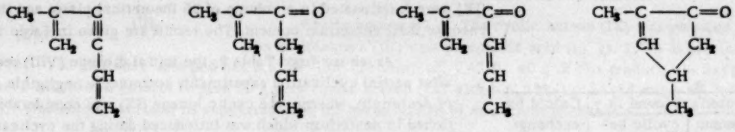
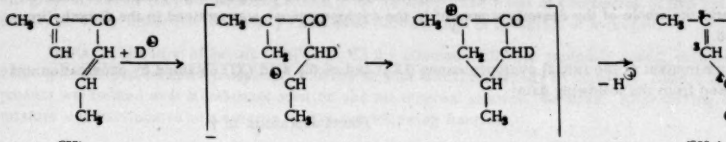
In the preceding communications [1, 2, 3] it was shown that the dienone formed by hydration of vinylisopropenylacetylene (I) cyclizes under the influence of acids to dimethylcyclopentenone (IV) by the ionic intermolecular mechanism proposed by Nazarov [4]. In this connection it was established that not only allylisopropenyl ketone (II) but also the isomeric propenylisopropenyl ketone (III) undergoes cyclization [3].



(I) (II) (III) (IV)

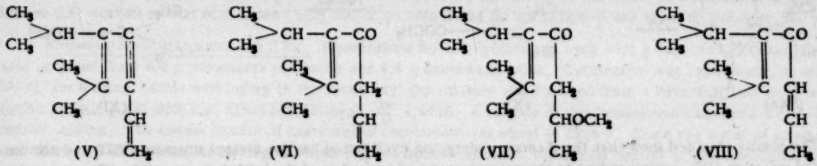
The ionic mechanism of cyclization of the dienone (III) into the cyclopentenone (IV) was verified by the method of labeled atoms with the help of deuterium [3]. Cyclization was effected with deuterophosphoric acid, and this gave monodeutero-dimethylcyclopentenone (IVa) which contains all the deuterium at the fifth carbon atom:



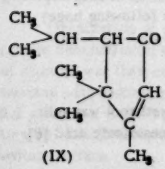
(III) (IVa)

As was shown by Nazarov and co-workers [5], also dienones of the type of (III) are easily amenable to cyclization. These compounds do not contain hydrogen atoms in the vinyl group at the end of the chain. In this case the resultant cyclopentenones contain a double bond at the 4,5-position.

We selected the dienone (VIII) for a study of the mechanism of cyclization of this type with the help of deuterium. This dienone is formed by hydration of the dienyne (V) under the influence of mercuric sulfate in aqueous methanol followed by cleavage of methanol from the methoxy ketone (VII) with the help of p-toluenesulfonic acid.



(V) (VI) (VII) (VIII)



(IX)

Cyclization of ketone (VIII), as shown by Nazarov and Pinkina [6], leads to trimethylisopropylcyclopentenone (IX).

The object of our investigation was to establish, when using deuterophosphoric acid for the cyclization of the initial dienone, whether the reaction proceeds by an intramolecular or by an ionic intermolecular mechanism. In the latter event, it was also desired to determine the point of introduction of deuterium into the molecule

of the resultant cyclic ketone (IX). The ionic intermolecular mechanism of cyclization of the initial dienone to the cyclopentenone (IX) could be rigorously demonstrated with the help of deuterium since monodeutero-cyclopentenone is formed on cyclization with deuterophosphoric acid.

That deuterium is actually introduced into the molecule of the cyclopentenone (IX) in the process of cyclization of the initial dienone (VIII) and not by way of deuterium exchange of these compounds was proved by special experiments. In the conditions of cyclization the cyclopentenone (IX) enters into exchange reaction with the deuterium-containing phosphoric acid only to a very slight extent, as can be seen from Table 1.

TABLE 1

Calculated for exchange of 1H, in γ	Deuterium found, in γ	Exchange, in %
1080	110	10
1030	70	7

Consequently, the cyclopentanone (IX) enters into exchange reaction in the conditions of cyclization to the extent of not more than 7-10% of that calculated for exchange of one hydrogen atom.

The exchange capacity of the initial dienone (VIII) proved to be still smaller, as was established by special experiments on incomplete cyclization of this dienone with deuterium-containing phosphoric acid. In these experiments the unreacted dienone (VIII) and cyclopentenone (IX) were fractionated in a column of 25 theoretical plates and then analyzed for their deuterium content. The results are given in Table 2.

TABLE 2

Expt. No.	Deuterium found, in γ		Calc'd for exchange of 1 H, in γ
	dienone (VIII)	cyclic ketone (IX)	
1	40	240	920
2	35	245	1050

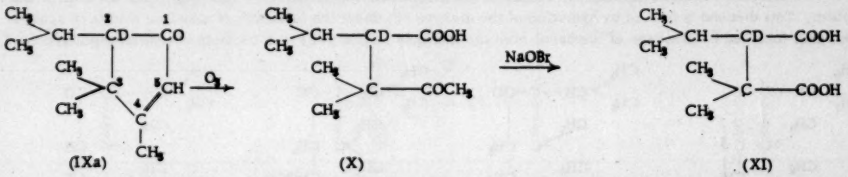
As we see from Table 2, the initial dienone (VIII) recovered after partial cyclization experiments contained a negligible amount of deuterium, whereas the cyclic ketone (IX) was considerably enriched in deuterium which was introduced during the cyclization process from the deuterium-enriched phosphoric acid.

The position of the deuterium in the cyclopentenone (IXa) was established by its ozonization to the ketoacid (X) which was then oxidized with bromide lye to dimethylisopropylsuccinic acid (XI). It was found that nearly the whole of the deuterium present in the cyclopentenone was retained in the dimethylisopropylsuccinic acid.

The deuterium content of the initial cyclopentenone (IXa) and of the acid (XI) obtained by ozonization and oxidation can be seen from the following data:

	Found deuterium in γ
Cyclic ketone (IXa)	70 100
Acid (XI)	62 100

It follows from these data that the deuterium introduced during the process of cyclization is present in the cyclic ketone (IXa) substantially entirely at C_3.



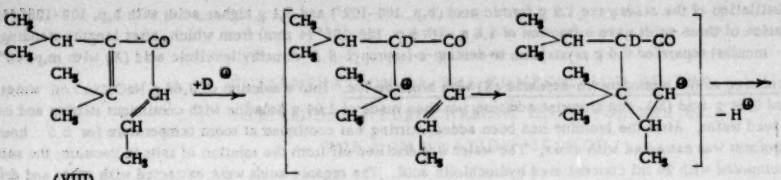
(IXa) (X) (XI)

The results obtained show that the dienone undergoing cyclization has the divinyl structure (VIII) and not the vinylallyl structure (VI), corresponding to the normal course of hydration of the initial dienyne (V). These experimental data lead to the following scheme for the mechanism of the cyclization reaction: (see following page)

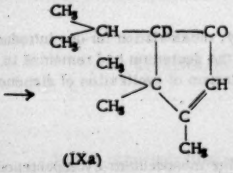
EXPERIMENTAL

Analyses for deuterium content were performed by the previously described method [7].

Preparation of dienone (VIII). The dienyne (V) was hydrated in aqueous methanol and methanol was split off from the 2-methoxy-5-isopropyl-6-methyl-5-hepten-4-one (VII) by heating with p-toluenesulfonic acid [6].



(VIII)



(IXa)

Distillation from a Favorsky flask gave a substance with b.p. 94-98° (12 mm); n_D^{20} 1.4715. The substance was then fractionated in a column packed with single glass helices with an efficiency of 25 theoretical plates. In this way from 44 g crude product was obtained 31 g pure dienone with b.p. 93-93.5° (12 mm); n_D^{20} 1.4735; d_4^{20} 0.8799; found MR 52.9; calculated MR 52.0. This dienone was used by us in the cyclization experiments.

Cyclic ketone (IX). The cyclic ketone (IX) was prepared by cyclization of dienone (VIII) with phosphoric acid (sp. gr. 1.76) as previously described [6]. The substance obtained had b.p. 98-100° (10 mm); n_D^{15} 1.4760. 40 g of this product was fractionated in the above-mentioned column to give 33 g pure cyclic ketone (IX) with b.p. 112-112.5° (17 mm); n_D^{20} 1.4779; d_4^{20} 0.9245. This ketone was used in experiments on the investigation of deuterium exchange.

Investigation of exchange ability of the cyclic ketone (IX). To 5.1 g cyclic ketone (IX) was added (from a dropping funnel) 5.55 g deuterium-enriched phosphoric acid (98%) with an excess density of 22,200 γ. After 2 hours' contact the mixture was gradually run into a solution of sodium bicarbonate and the cyclic ketone was extracted with ether. After drying the ethereal solution, driving off the ether and distilling the product in vacuum, 4.5 g cyclic ketone (IX) was obtained with b.p. 93° (8 mm). The water of combustion of this ketone had an excess density of 110 γ instead of the 1080 γ calculated for exchange of one atom of hydrogen.

Partial cyclization of ketone (VIII). To 23.0 g dienone (VIII) was gradually added, with cooling and stirring, 21.25 g deuterium-enriched phosphoric acid (98%) with an excess density of 22,200 γ. After 2 hours' contact the product was treated with bicarbonate solution and the ethereal solution was dried. After driving off the ether, the mixture was fractionated in a column to give the following fractions:

Fraction I, b.p. 89.1-89.4° (12 mm); n_D^{20} 1.4729; 4.5 g
Fraction II, b.p. 91.0-91.4° (12 mm); n_D^{20} 1.4732; 2.0 g
Fraction III, b.p. 91.4-101.2° (12 mm); n_D^{20} 1.4750; 1.5 g
Fraction IV, b.p. 101.2-102.8° (12 mm); n_D^{20} 1.4777; 6.5 g

Fraction IV is the cyclic ketone (IX). The water of combustion of this ketone had an excess density of 240 γ. Fraction I is the original dienone (VIII). Its water of combustion had an excess density of 26 γ. The excess density of the water of combustion of Fraction III was 50 γ. Calculated for exchange of one atom of hydrogen 1050 γ. Similar results were obtained on repeating this experiment – the excess density of the water of combustion of the cyclic ketone (IX) was 240 γ, that of dienone (VIII) was 40 γ; calculated for exchange of one atom of hydrogen 920 γ.

Monodeutero-cyclopentenone (IXa). Components for the cyclization were 14.4 g dienone (VIII) and phosphoric acid prepared from 9.6 g phosphorus pentoxide and 4.4 g deuterium oxide. Cyclization was carried out, as usual, at 20-21° for 8 hours. After working up in the usual way, the mixture was distilled from a Favorsky flask to give 12 g cyclic ketone (IXa) with b.p. 113-114° (18 mm); n_D^{20} 1.4776. A sample of this ketone was examined for its deuterium content. The excess density of the water of combustion was equal to 3895 γ. Since the water of combustion was diluted 18 times with the hydrogen-atoms present in the molecule, the excess density of one introduced hydrogen was equal to 3895 · 18 = 70,100 γ.

Ozonization of monodeutero-cyclopentenone (IXa). Ozonized oxygen was passed at the rate of 3-4 liters/hour (ozone concentration 6%) for 16 hours into a solution of 10 g cyclic ketone (IXa) in 45 ml dry chloroform. The solution of ozonide was then run into 20 ml water and stirred for 34 hours at a temperature of 60-65°. The acids were neutralized with sodium carbonate (11.5 g). The neutral products were extracted with ether. Removal of the ether left 2.2 g viscous, dark-brown liquid. The water was driven off from the solution of salts in vacuum and the salts were treated with 25 ml concentrated hydrochloric acid. The organic acids were extracted with ether and dried with sodium sulfate.

Distillation of the acids gave 1.2 g formic acid (b.p. 100-102°) and 5.1 g higher acids with b.p. 100-125° (4mm). Redistillation of these acids gave a fraction of 1.8 g with b.p. 120-125° (4 mm) from which, after lengthy standing (1-1.5 months) separated 0.4 g crystalline α-deutero-α-isopropyl-β,β-dimethyllevulinic acid (X) with m.p. 48° [6].

Oxidation of the monodeutero-ketoacid (X) with bromide lye. Into a solution of 0.66 g NaOH in 7 ml water was introduced 0.34 g acid (X), and dropwise addition was then made of 1.04 g bromine with continuous stirring and cooling with iced water. After the bromine had been added, stirring was continued at room temperature for 3.5 hours. The bromoform was extracted with ether. The water was distilled off from the solution of salts in vacuum; the salts were decomposed with 20 ml concentrated hydrochloric acid. The organic acids were extracted with ether and dried with sodium sulfate. After removal of the ether, the residue was recrystallized from hot water. Yield 202 mg α-deutero-α-isopropyl-β,β-dimethylsuccinic acid (XI) with m.p. 134-135° [6].

The water obtained on combustion of this acid had an excess denisty of 3880 γ; recalculation for one introduced hydrogen gives a value of 3880 · 16 = 62,100 γ. Consequently, nearly the whole of the deuterium had remained in the molecule of acid (XI). This, convincingly, shows the correctness of the ionic mechanism of cyclization of dienone (VIII) advanced in the theoretical part of this paper.

SUMMARY

1. Under the action of deuterophosphoric acid the dienone (VIII) cyclizes to the monodeutero-cyclopentenone (IXa) which, on ozonization, gives the deutero-ketoacid (X); oxidation of the latter with bromide lye leads to the deutero-dicarboxylic acid (XI).

2. The dienone (VIII) and the cyclic ketone (IX) practically do not exchange their hydrogens for deuterium in the conditions of cyclization and, consequently, the entry of deuterium into the molecule of the cyclic ketone only takes place in the instant of its cyclization.

3. The results obtained are convincing evidence of the correctness of the proposed ionic mechanism of this cyclization reaction.

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Received October 19, 1953

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* T.p. = C.B. English translation pagination.

DETERMINATION OF THE COMPOSITION OF THE INDIVIDUAL HYDROCARBONS OF GASOLINES BY THE COMBINATION METHOD

COMMUNICATION 5. GASOLINE FROM EMBA PETROLEUM

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In this communication we submit the results of an investigation of the individual hydrocarbon composition of a gasoline with an end boiling point of 150° from the low-sulfur Emba petroleum of the Koschagyl deposit from hole No. 6 of the 1949 strike. The investigation was carried out by the previously described combination method [1], used for examination of two gasolines from petroleums from the Kazanbulaksky deposit [2], two Suransk gasolines [3] and a gasoline from a Taimazinskoil [4]. As in the case of the gasolines from the Kazanbulaksky and Taimazinsk oils, the gasoline investigated in the present research was obtained by fractional distillation in the laboratory.

As a result of the investigation, the composition of the gasoline from Emba oil was accounted for to the extent of 81.1%. It was found to contain in all 50 hydrocarbons, which were determined quantitatively. Their distribution by classes is set forth in Table 1.

TABLE 1
Distribution by Classes of the Hydrocarbons Found

Class of hydrocarbon	No. hydrocarbons in gasoline
Paraffins	22
Cyclopentanes	9
Cyclohexanes	13
Aromatics	6
	50

In the further discussion the gasoline from Emba oil will, for brevity, be called TsE-1. The system for designation of the fractions by letters is the same as in the previous investigations [1-4]. All the individual hydrocarbons found in the gasoline are calculated in percentages by weight of the whole gasoline and set forth in Table 2. The same table gives the total material balance of the whole investigation. The data of Table 2 permit the establishment of the group composition of the gasoline, taking into account the individual paraffins with normal and branched structures, as well as the individual cyclopentane and cyclohexane hydrocarbons. This is illustrated in Table 3.

As we see from Tables 2 and 3 (Table 2 on next page), the gasoline from Emba petroleum is predominantly naphthenic (56.1%). The ratio between the amounts of cyclopentanic and cyclohexanic hydrocarbons is 0.48.

Only 21.8% of the paraffinic hydrocarbons out of the total amount of paraffins have a normal structure and these are mainly lower molecular paraffins (C_3, C_4, C_5, and C_6). Of the isoparaffins present, 88% possess a tertiary carbon atom and 12% a quaternary carbon atom. Consequently hydrocarbons with a tertiary carbon atom predominate among the branched-chain paraffins. The greater proportion (approx. 75%) of all the isoparaffins with tertiary carbon atoms have only one side chain, while the remainder each have two side chains.

TABLE 3
Group Composition of Gasoline TsE-1

Hydrocarbons	Content in weight % of the gasoline
Normal paraffins	4.8
Paraffins with a tertiary carbon atom	15.3
Paraffins with a quaternary carbon atom	2.1
Cyclopentanes	18.3
Cyclohexanes	37.8
Aromatics	2.8

TABLE 2

Individual Hydrocarbons Found in Gasoline TsE-1

Hydrocarbon	Content, in wt-% of the TsE-1	Hydrocarbon	Content, in wt-% of the TsE-1
Paraffin hydrocarbons			
Propane	0.18	2,2-Dimethylpentane	0.66
n-Butane	1.75	2,3-Dimethylpentane	1.99
Isobutane	1.28	2,4-Dimethylpentane	0.33
n-Pentane	1.77	3,3-Dimethylpentane	0.60
2-Methylbutane	3.55	n-Octane	0.43
Neopentane	0.13	3-Methylheptane	1.07
n-Hexane	0.70	4-Methylheptane	0.54
2-Methylpentane	1.77	2,2-Dimethylhexane	0.15
3-Methylpentane	1.27	2,4-Dimethylhexane	0.59
2,2-Dimethylbutane	0.55	3-Methyloctane	0.82
2,3-Dimethylbutane	0.96	4-Methyloctane	1.10
		Total	22.2
Cyclopentane hydrocarbons			
Cyclopentane	0.32	cis-1,3-Dimethylcyclopentane	1.59
Methylcyclopentane	3.51	trans-1,3-Dimethylcyclopentane	1.99
Ethylcyclopentane	0.99	1,2,3-Trimethylcyclopentane	2.52
1,1-Dimethylcyclopentane	0.88	1,2,4-Trimethylcyclopentane	4.10
Trans-1,2-dimethylcyclopentane	2.39	Total	18.3
Cyclohexane hydrocarbons			
Cyclohexane	4.64	1-Methyl-2-ethylcyclohexane	0.39
Methylcyclohexane	13.06	1-Methyl-3-ethylcyclohexane	0.58
Ethylcyclohexane	1.89	1-Methyl-4-ethylcyclohexane	0.58
1,1-Dimethylcyclohexane	0.98	1,1,3-Trimethylcyclohexane	3.39
1,2-Dimethylcyclohexane	2.27	1,2,4-Trimethylcyclohexane	0.97
1,3-Dimethylcyclohexane	6.19	1,3,5-Trimethylcyclohexane	0.58
1,4-Dimethylcyclohexane	2.27	Total	37.8
Aromatic hydrocarbons			
Benzene	0.04	Other cyclohexane hydrocarbons of the composition C_9H_{18} (not identified)	(0.78)
Toluene	0.54	Remained unidentified	81.1
Ethylbenzene	0.12	Sulfur compounds and losses	7.58
o-Xylene	0.54		0.96
m-Xylene	1.18	Losses	7.94
p-Xylene	0.42	Residues in flask during fractionation	2.38
Total	2.8	Total in % of the TsE-1	100.0

Inspection of the composition of the paraffins by groups of hydrocarbons with identical molecular weight shows that all the possible isomers of C_5 and C_6 hyrocarbons are found in the gasoline. Of the C_7 hydrocarbons in this gasoline, only all the possible dimethylpentanes are present. The C_8 hydrocarbons found are n-octane (although in very small amount – 0.43%) and two methylheptanes (2-methylheptane not found). Of the isooctanes with two side chains, only two isomers were found: 2,2- and 2,4-dimethylhexanes. Highly branched isooctanes are completely absent from

TsE-1. Of the C_9 hydrocarbons, two representatives are found: 2- and 3-methyloctanes. Consequently, with increasing molecular weight the number of different isomers of hydrocarbons of the paraffin series and the total content of paraffinic hydrocarbons of identical molecular weight decrease.

The cyclopentane content of the gasoline is insignificant. Among the cyclopentanic hydrocarbons with one side chain, methylcyclopentane predominates. Of the cyclopentanic hydrocarbons with two side chains present in the gasoline, apart from cis-1,2-dimethylcyclopentane, all the possible dimethylcyclopentanes are represented, including 1,1-dimethylcyclopentane. It should be pointed out that, as seen in Table 2, among the dimethylcyclopentanes, the trans-forms in all cases predominate over the cis-forms. In addition to dimethylcyclopentanes, TsE-1 gasoline contains a considerable amount of trimethylcyclopentanes. With increasing molecular weight of the cyclopentanic hydrocarbons, their content in TsE-1 gasoline rises.

The content of cyclohexanic hydrocarbons in TsE-1 gasoline is double that of the cyclopentanic hydrocarbons (37.8% against 18.3%). A noteworthy feature is the relatively high content of methylcyclohexane (13.06%) in comparison with the other representatives of the hydrocarbons of this class. The most plentiful representative of the cyclohexanes with two methyl groups in the gasoline is 1,3-dimethylcyclohexane; 1,2- and 1,4-dimethylcyclohexanes are present in identical amounts. Among the methylethylcyclohexanes the hydrocarbons with side chains in the 1,3-position again predominate. Among the trimethylcyclohexanes 1,1,3-trimethylcyclohexane with a quaternary carbon atom predominates. The percentage content of cyclohexanic hydrocarbons rises insignificantly with increasing molecular weight.

The aromatics content of TsE-1 gasoline (2.8%) is very low in comparison with the other classes of hydrocarbons. The content of individual aromatic hydrocarbons falls off in the following order: m-xylene, toluene, o-xylene, p-xylene, ethylbenzene and benzene. Here, as in the case of cyclohexanic hydrocarbons, there is a noteworthy predominance of hydrocarbons with one side chain or with two side chains in the meta-position. Furthermore, as in the case of cyclopentanic hydrocarbons, a sharp rise is observed in the percentage content of aromatic hydrocarbons with rising molecular weight.

EXPERIMENTAL

Preparation of a broad cut of ShE-1 and its fractionation. The oil in copper stills was distilled off to give a ShE-1 fraction with an end boiling point of 200°. The evolved hydrocarbon gases were collected in traps cooled to −70°, and at the conclusion of the fractionation they were added to the distillate. The resultant ShE-1 fraction had the following characteristics: n_D^{20} 1.4245; d_4^{20} 0.7579; aniline point 51.3°; sulfur content 0.024* weight-%.

The results of fractionation of the broad cut in a column with an efficiency of 25 theoretical plates are set forth in Table 4 and Fig. 1. The AE -1 fraction had the following characteristics: n_D^{20} 1.4170; d_4^{20} 0.7561; aniline point 48.2°, sulfur content 0.0106 weight-%. Subsequently, all the calculations of content of individual hydrocarbons and fractions obtained at separate stages of the investigation were carried out on the complete TsE-1 gasoline, comprising fractions K_1, L and A, i.e. all fractions boiling up to 150°. This TsE-1 fraction weighted 1392.2 g.

TABLE 4

Results of Fractionation of ShE-1 Gasoline

Fraction	Boiling limits in °C (760 mm)	Weight in g	Content of fraction in weight-%	
			on ShE-1	on TsE-1
Taken for distillation	–	2005	100.0	
Gaseous portion K_1E-1	–	59	2.94	4.24
Light fraction LE-1	21.8 - 54.9	89	4.44	6.39
Main fraction AE-1	54.9 -150.1	1244	62.04	89.355
Residue	Above 150.1	594	29.63	–
Losses	–	19	0.95	–

Examination of gases and light fraction (K_1 and L). The gaseous portion K_1E-1 and the light fraction LE-1 contained sulfur compounds. For the purpose of eliminating the readily volatile sulfur compounds, the ampoule containing the gaseous fraction K_1E-1 was connected to a train of absorbers comprising a sodium hydroxide washer, a bubbler containing sulfuric acid, a silica gel column and spiral tube traps cooled with liquid air. The gases were slowly passed through this system and condensed in the spiral traps. Nitrogen was passed through the system to purge

* The sulfur content was determined by the method of combusion in a lamp.

out the gaseous hydrocarbons. After weighing the ampoule and the spiral traps before and after the experiment, the ampoule containing fraction L, which had been heated to +30° toward the end of the experiment, was connected to the same system. The gas liberated in this way was collected in the same traps together with the gas from the gaseous fraction K_1, and was likewise purged from the system with nitrogen. The combined lots of purified gas were designated by the letter K_1', while the combined non-evaporated residues were designated by L'. Results of experiments on purification of the bases of fractions K_1 and L from sulfur compounds are set forth in Table 5.

TABLE 5

Results of Purification of K_1E-1 Gases from Sulfur Compounds

Fractions	Weight in g			Content of fractions, in weight-%	
	K_1E-1	LE-1	Total	On K_1 L	On TsE-1
Taken for purification	59.2	89.0	148.2	100.0	10.63
Gas K_1'E-1	50.5	0.70	51.2	34.55	3.67
Light fraction L'E-1	7.04	86.83	93.8	63.29	6.73
Sulfur compounds and losses	1.70	1.50	3.2	2.16	0.23

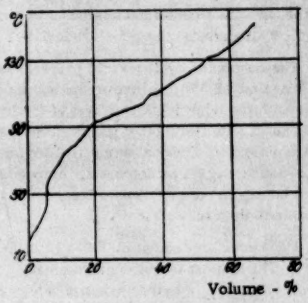

Fig. 1. Curve of fractionation of ShE-1

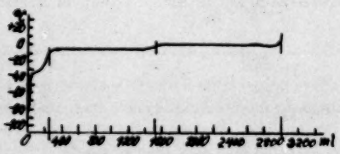

Fig. 2. Curve of fractionation of KE-1 in a Podbielniak column

Fractionation of the purified gas K' was carried out in a Podbielniak column. Results of the fractionation are set forth in Table 6 and in Fig. 2.

TABLE 6

Results of Fractionation of K'E-1 Gas

Hydrocarbon	Weight in g	Content of hydrocarbons in weight-%	
		on K'E-1	on TsE-1
Taken for fractionation	8.68	100.0	3.67
Propane	0.429	4.94	0.18
Isobutane	3.036	34.93	1.28
n-Butane	3.448	39.72	1.46
Neopentane	0.058	0.67	0.02
Residue with b.p. above +16°	1.35	15.55	0.57
Losses	0.36	4.15	0.15

The residue after fractionation of the gas with b.p. above +16° was not combined with the light cut L' due to its small amount (as specified in the scheme [1]); its quantitative composition was evaluated on the basis of the refractive index of n_D^{20} 1.3541; it contained in weight-%:

	On residue	On TsE-1
Isopentane	88.85	0.51
n-Pentane	11.15	0.06

The light cut L'E-1 of the gasoline likewise contained sulfur compounds. The latter were removed by chromatographic adsorption. The fraction was passed at a temperature of −10 to −45° through an adsorption column filled with silica gel and was eluted first with ethanol and then with water. Results of these experiments are set forth in Table 7.

Distillation of the gas (debutanization) from the desulfurized light cut was carried out again in a Podbielniak column. Results of the fractionation are set forth in Table 8.

Examination of debutanized fraction ME-1. Fraction ME-1 was fractionated in a column with an efficiency of 40 theoretical plates. The fractionation curve (Fig. 3) was plotted simultaneously with the collection of the cuts.

TABLE 7

Results of Adsorptive Separation of Sulfur Compounds from Light Fraction L'E-1

Fraction	Weight in g	Content of fraction, in weight-%	
		on fraction L'E-1	on TsE-1
L'E-1 passed through	36,05	100,0	6,73
Desulfurized light fraction L'_1E-1	35,16	97,53	6,56
Sulfur compounds and losses	0,89	2,47	0,17

TABLE 8

Results of Debutanization and Fractionation of Desulfurized Light Fraction L'_1E-1

Hydrocarbon	Weight in g	Content of hydrocarbons, in weight-%	
		on L'_1E-1	on TsE-1
Taken for fractionation	33,15	100,0	6,56
n-Butane	1,56	4,44	0,29
Neopentane	0,54	1,54	0,10
Debutanized light cut	32,50	92,46	6,07
Losses	0,55	1,56	0,10

The amount of fractions and their properties are set forth in Table 9. The constants of fraction I are seen to correspond perfectly to those of pure 2-methylbutane (b.p. 27,85°; n_D^{20} 1,3537 and d_4^{20} 0,6197) while the constants of fraction II are close to those of pure n-pentane (b.p. 36,07°, n_D^{20} 1,3575, d_4^{20} 0,6262). Consequently the amounts of fractions obtained represent the contents of these hydrocarbons in the gasoline.

The residue of fraction ME-1, as shown by an examination of the Raman spectrum, has the following composition:

Content, in weight-%

	On residue	On TsE-1
2,2-Dimethylbutane	40	0,43
Cyclopentane	30	0,32
2-Methylpentane	20	0,21
n-Pentane	10	0,11

Separation of aromatic hydrocarbons from the mixture of paraffins and naphthenes in main fraction AE-1. Fraction AE-1 was subjected to chromatographic adsorptive resolution into the aromatic BE-1 fraction and the paraffin-naphthenic fraction VE-1. Since the aromatic content of fraction A is low (6%), the adsorptive resolution was carried out with isolation of an intermediate fraction. Complete resolution was achieved by a fresh chromatographic adsorption of the intermediate fraction using pentane as the displacement liquid. Results of the separation are set forth in Table 10.

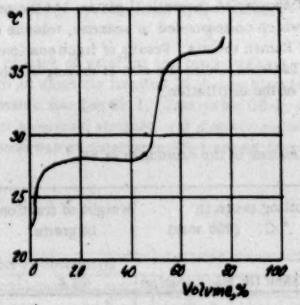

Fig. 3. Curve of fractionation of ME-1

TABLE 9

Results of Fractionation of the Light Cut ME-1

Boiling range in °C (760 mm)	Weight in g	n_D^{20}	d_4^{20}	Aniline pt. in °C	Content of fraction in weight-%	
					on ME-1	on TsE-1
Taken for fractionation	31,6	–	–	–	100,0	6,07
20,0-32,0	15,8	1,3540	0,6190	76,8	50,00	3,04
32,0-37,7	8,3	1,3574	0,6252	71,1	26,27	1,60
Residue	5,5	1,3792	0,6732	59,7	17,56	1,07
Losses	1,9				6,17	0,37

Table 10 gives both the actual amounts of fractions isolated and the corrected amounts; the latter were obtained by adding to the actual amount those amounts of the fractions which were used up in carrying out qualitative reactions for aromatic hydrocarbons and for determination of the refractive index.

The dearomatized fraction V did not contain sulfur. Aromatic fraction B contained about 0,02% sulfur, representing approximately 7% of all the sulfur present in the original gasoline A.

TABLE 10
Chromatographic Resolution of Fraction AE-1

Amount of fraction AE-1 taken in g	Results of resolution										
	aromatics BE-1				paraffin-naphthene portion VE-1				losses		
	actual in g	corrected in g	% on the AE-1	% on TsE-1	actual in g	corrected, in g	% on the AE-1	% on TsE-1	in g	% on the AE-1	% on the TsE-1
1146.3	42.9	43.3	3.8	3.37	1095.1	1095.77	95.6	85.41	7.3	0.63	0.56

The isolated fractions had the following constants and analyses:

	n_D^{20}	d_4^{20}	Aniline pt., in °C	Sulfur content, in wt-%
BE-1	1.4902	0.8536	—	~0.02
CE-1	1.4152	0.7505	51.2	0

Examination of aromatics of CE-1 The aromatic hydrocarbons of BE-1 were fractionated in a column with an efficiency of approx. 40 theoretical plates. At the same time a fractionation curve was plotted and fractions were collected which corresponded to benzene, toluene and xylenes. The xylene fraction (III) was investigated with the help of Raman spectra. Results of fractionations, properties of fractions and results of optical analysis are set forth in Table 11. With the aim of driving off the whole of the xylene fraction, pure decalin was added toward the end of the distillation.

TABLE 11
Results of Fractionation of the Aromatics of BE-1

Fraction	Boiling range, in °C (760 mm)	Weight of fraction, in grams	n_D^{20}	d_4^{20}	Content of fraction, in wt-%	
					on BE-1	on TsE-1
	Taken for fractionation	38.6	1.4902	0.8536	100.00	3.37
I	89.2-103.7	0.45	1.4543	0.7811	1.17	0.04
II	103.7-127.9	6.1	1.4768	0.8312	15.80	0.54
III	127.9-150.0	28.2	1.4941	0.8607	73.06	2.46
	Residue	1.4			3.63	0.12
	Losses	2.45			6.35	0.21

It is seen from the data that the physical properties of fraction I identify it with benzene, while those of fraction II correspond to toluene. We may therefore assume that the amounts of these two fractions correspond to the content of benzene and toluene in the gasoline.

Results of optical analysis of fraction III

	Content of hydrocarbon, in weight-%	
	On fraction III	On TsE-1
o-Xylene	22	0.54
m-Xylene	48	1.18
p-Xylene	17	0.42
Ethylbenzene	5	0.12
Not identified	8	0.20

The presence of sulfur compounds in the aromatic fractions interfered with the sharpness of the fractionation and was reflected in the constants found for the hydrocarbons.

Dehydrogenation of the cyclohexanic hydrocarbons. The paraffin-naphthenic fraction V was subjected to dehydrogenation for conversion of the cyclohexane hydrocarbons into aromatics. Fraction V was passed over an iron-platinum catalyst at 300° at a velocity of 0.8-1.0 liters/liter· hour continuously for 24 hours. The results obtained are set forth in Table 12.

TABLE 12

Dehydrogenation of the Paraffin-Naphthenic Fraction VE-1

Fraction	Amount of fraction VE-1 taken, in g	Fraction GE-1 obtained				Hydrogen and losses		
		actual, in g	corrected, in g	in wt.-%		in g	in % of VE-1	in % of TsE-1
				on VE-1	on TsE 1			
BE-1	748.0	704.4	704.4	94.17	80.43	43.6	5.83	4.98

In this table the corrected amounts of catalyzate G were obtained by adding to the actual amounts of G those amounts of the latter which had been used up in determining the refractive index. The losses include the hydrogen liberated on dehydrogenation of the hexamethylenes whose amount was not determined.

The physical properties of the original fraction V and of the catalyzate G obtained after dehydrogenation are as follows:

	n_D^{20}	d_4^{20}	Aniline point, °C
VE-1	1.4152	0.7505	51.2
GE-1	1.4413	0.7840	+15.4

The physical properties of the catalyzate indicate that gasoline from Emba petroleum contains a considerable amount of cyclohexanic hydrocarbons.

Resolution of catalyzate GE-1 into aromatics and a mixture of paraffins and cyclopentanes. Catalyzate GE 1 was subjected to chromatographic adsorptive resolution into an aromatic fraction DE-1 (resulting from dehydrogenation of the cyclohexanic hydrocarbons) and a paraffin-cyclopentanic fraction ES-1. Catalyzate GE-1, which contained approx. 40% aromatic hydrocarbons (this was determined on a separate sample), was directly eluted with isopentane without isolation of an intermediate fraction. Results of resolution of catalyzate GE-1 are set forth in Table 13.

TABLE 13

Chromatographic Resolution of Catalyzate GE-1

Amount taken of catalyzate GE-1, in g	Results of Resolution										
	Aromatics DE-1				Paraffin cyclopentanic portion EE-1				Losses		
	actual, in g	corrected, in g	in % of GE-1	in % of TsE-1	actual, in g	corrected, in g	in % of GE-1	in % of TsE-1	in g	in % of GE-1	in % of TsE-1
539.7	216.8	221.3	41.00	32.98	301.2	301.2	55.81	44.89	17.20	3.19	2.57

After the isopentane had been driven off the isolated fractions DE-1 and EE-1 had the following constants:

	n_D^{20}	d_4^{20}	Aniline point, °C
DE-1	1.4966	0.8659	–
EE-1	1.4073	0.7352	57.9

Investigation of Aromatics D. The aromatic hydrocarbons DE-1, obtained by dehydrogenation of the cyclohexanic hydrocarbons, were fractionated in a column with an efficiency of about 40 theoretical plates (in a similar manner as for aromatics B). Results of the fractionation, properties of the fractions and results of optical analysis are set forth in Table 14. The table also includes the results of recalculation of the amounts of isolated aromatic fractions to the corresponding amounts of cyclohexanic hydrocarbons present in the original gasoline.

Investigation of the paraffin-cyclopentanic fraction EE-1. The paraffin-cyclohexanic fraction EE-1 was freed from isopentane and fractionated in a column with an efficiency of 50 theoretical plates into narrow cuts. Previously with the same column a curve was plotted of the fractionation of 100 ml EE-1 fraction with continuous collection of distillate with a reflux number of 45-50. The fractionation curve of EE-1 is shown in Fig. 4. The vertical strokes designate the limits of subsequent taking-off of narrow cuts whose selection was governed by the character of the fractionation curve and by the boiling points of the individual hydrocarbons.

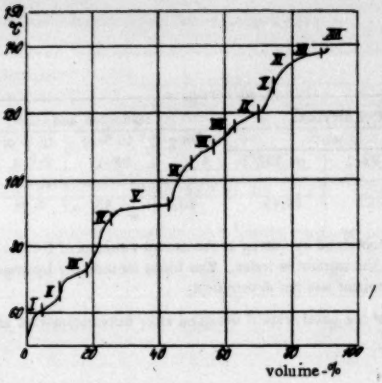

Fig. 4. Curve of fractionation of EE-1

After the fractionation curve had been plotted, 300 ml of fraction EE-1 was fractionated into narrow cuts in the same column with continuous take-off of distillate and with a reflux number of 40-45. In all 13 narrow cuts were collected. Results of the fractionation of the paraffin-cyclopentanic fraction E into narrow cuts are set forth in Tables 15 and 16 together with the properties of the obtained cuts and the data of a Raman spectroscopic investigation of the cuts. The data for optical analysis of the cuts are in accord with their physical properties.

Table 2 presents all the data, in percentages by weight of TsE-1 gasoline, on the composition of the individual hydrocarbons it contains, as determined in the course of the present research. The overall results of the study are also adduced in the same table.

Laboratory assistants T.V.Lapshina, V.A.Ovodova, K.G. Ryabova and G.S.Taits participated in this research.

TABLE 14

Results of Fractionation of Aromatics DE-1

Fractions	Boiling range, in ° C (760 mm)	Weight of fraction, in grams	n_D^{20}	d_4^{20}	Content of fraction, in wt-% of DE-1	Content of corresponding cyclohexanes, in wt-% of TsE-1
	Taken for fractionation	61.1	1.4966	0.8659	100.00	
I	78.4-100.0	7.5	1.4971	0.8712	12.27	4.36
II	100.0-128.0	22.0	1.4953	0.8641	36.01	12.64
III	128.0-150.0	22.15	1.4970	0.8655	36.25	12.63
IV	150.0-173.5	6.85	1.4980	0.8695	11.21	3.89
	Residue	0.45			0.74	0.25
	losses	2.15			3.52	1.23
					Total	35.00

Aromatic hydrocarbons (1)	Content, as weight-% of fraction III (2)	Cyclohexanic hydrocarbons (3)	Content, as wt-% of TsE-1 (4)
Results of optical analysis of fraction III			
o-Xylene	18	1,2-Dimethylcyclohexane	2.27
m-Xylene	49	1,3-Dimethylcyclohexane	6.19
p-Xylene	18	1,4-Dimethylcyclohexane	2.28
Ethylbenzene	15	Ethylcyclohexane	1.89

TABLE 14 (cont.)

(1)	(2)	(3)	(4)
	Results of optical analysis of fraction IV		
1-Methyl-2-ethylbenzene	10	1-Methyl-2-ethylcyclohexane	0,39
1-Methyl-3-ethylbenzene	15	1-Methyl-3-ethylcyclohexane	0,58
1-Methyl-4-ethylbenzene	15	1-Methyl-4-ethylbenzene	0,58
1,2,4-Trimethylbenzene	25	1,2,4-Trimethylcyclohexane	0,97
1,3,5-Trimethylbenzene	15	1,3,5-Trimethylcyclohexane	0,58
Unidentified	20		0,79

TABLE 15

Results of Fractionation of the Paraffin-cyclopentanic Fraction EE-1

Fractions	Boiling range in °C (760 mm)	Weight of fraction in grams	Content of fraction in weight-%		n_D^{20}	d_4^{20}	Aniline point in °C
			of EE-1	of TsE-1			
	Taken for fractionation of E	220,5	100,0	44,89	1,4073	0,7352	57,9
I	48,2-62,0	11,8	5,35	2,40	1,3749	0,6617	70,1
II	62,0-67,8	7,8	3,54	1,59	1,3762	0,6638	69,0
III	67,8-74,0	20,3	9,21	4,13	1,4021	0,7296	41,1
IV	74,0-89,0	13,5	6,12	2,75	1,3985	0,7161	57,9
V	89,0-92,5	39,1	17,73	7,96	1,4040	0,7298	54,3
VI	92,5-105,0	13,9	6,30	2,83	1,4098	0,7412	52,9
VII	105,0-110,0	15,1	6,85	3,07	1,4082	0,7374	62,1
VIII	110,0-116,5	13,7	6,21	2,79	1,4095	0,7385	62,3
IX	116,5-120,0	17,6	7,98	3,58	1,4122	0,7409	60,5
X	120,0-128,5	10,7	4,85	2,18	1,4180	0,7567	57,3
XI	128,5-135,0	8,2	3,72	1,67	1,4175	0,7549	62,7
XII	135,0-138,0	23,7	10,75	4,83	1,4215	0,7626	61,4
XIII	138,0-144,3	13,5	6,12	2,75	1,4182	0,7022	64,8
	Residue	9,9	4,49	2,01			
	Losses	1,7	0,77	0,35			
			99,99	44,89	—	—	—

SUMMARY

1. Gasoline with an end boiling point of 150°, obtained from low-sulfur Emba petroleum (Koschagyl), was analyzed with the help of the combination method of investigation of the individual hydrocarbons of straight-run gasolines.

TABLE 16

Results of Optical Investigation of the Narrow Cuts of the Paraffin-Cyclopentanic Fraction EE-1

Hydrocarbons found by the optical method	Content of hydrocarbons in wt-% of fraction	Content of hydrocarbons in wt-% of TsE-1	Hydrocarbons found by the optical method	Content of hydrocarbons, in wt-% of fraction	Content of hydrocarbons, in wt-% of TsE-1
Fraction I			**Fraction VII**		
2,2-Dimethylbutane	5	0.12	2,2-Dimethylhexane	~5	0.15
2,3-Dimethylbutane	40	0.96	2,4-Dimethylhexane	10	0.31
2-Methylpentane	55	1.32	1,2,4-Trimethylcyclopentane	60	1.84
			1,2,3-Trimethylcyclopentane	~25	0.77
Fraction II			**Fraction VIII**		
2-Methylpentane	15	0.24	1,2,4-Trimethylcyclopentane	30	0.84
3-Methylpentane	80	1.27	2,4-Dimethylhexane	~10	0.28
n-Hexane	5	0.08	1,2,3-Trimethylcyclopentane	~50	1.39
			Not identified	~10	0.28
Fraction III			**Fraction IX**		
n-Hexane	15	0.62	4-Methylheptane	15	0.54
Methylcyclopentane	85	3.51	3-Methylheptane	30	1.07
			1,1-Dimethylcyclohexane	15	0.54
Fraction IV			1,2,3-Trimethylcyclopentane	10	0.36
2,2-Dimethylpentane	24	0.66	Not identified	30	1.07
2,4-Dimethylpentane	~12	0.33			
Cyclohexane	~10	0.28	**Fraction X**		
3,3-Dimethylpentane	22	0.60	1,1-Dimethylcyclohexane	20	0.44
1,1-Dimethylcyclopentane	32	0.88	n-Octane	20	0.43
			Not identified	60	1.31
Fraction V			**Fraction XI**		
2,3-Dimethylpentane	25	1.99	1,1,3-Trimethylcyclohexane	25	0.42
cis-1,3-Dimethylcyclopentane	20	1.59	Not identified	75	1.25
trans-1,3-Dimethylcyclopentane	25	1.99	**Fraction XII**		
trans-1,2-Dimethylcyclopentane	30	2.39	1,1,3-Trimethylcyclohexane	50	2.42
			Not identified	50	2.41
Fraction VI			**Fraction XIII**		
Methylcyclohexane	~15	0.42	1,1,3-Trimethylcyclohexane	20	0.55
Ethylcyclopentane	35	0.99	3-Methyloctane	30	0.82
1,2,4-Trimethylcyclopentane	30	1.42	4-Methyloctane	40	1.10
			Not identified	10	0.28

2. The individual hydrocarbon composition of gasoline from Emba petroleum was established to the extent of 81.1 weight-% of the total gasoline. Total losses were approx. 8%.

3. It was found that the investigated gasoline from Emba petroleum was naphthenic. Among the paraffinic hydrocarbons the branched-chain compounds predominate. Among the cyclopentanic hydrocarbons the chief representative is methylcyclopentane, and a series of hydrocarbons is present with two and three side chains. The cyclohexanic hydrocarbons present in largest quantity are methylcyclohexane, 1,3-dimethylcyclohexane and 1,1,3-trimethylcyclohexane. m-Xylene predominates among the aromatic hydrocarbons.

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Received December 19, 1953

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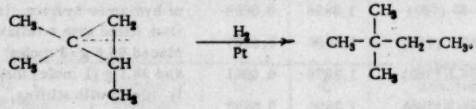
SYNTHESIS AND CATALYTIC HYDROGENOLYSIS OF 1,1,2-TRIMETHYLCYCLOPROPANE

B. A. Kazansky, M. Yu. Lukina and V. A. Ovodova

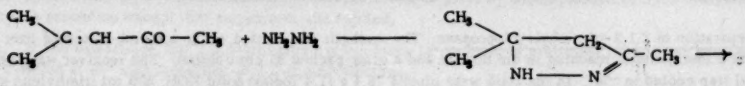
Continuing our study of the behavior of hydrocarbons of the cyclopropane and cyclobutane series in the conditions of catalytic hydrogenolysis over platinized carbon, we subjected 1,1,2-trimethylcyclopropane to hydrogenolysis.

It was found that the three-membered 1,1,2-trimethylcyclopropane ring is completely ruptured by a single pass of the hydrocarbon at a space velocity of 0.4 through a tube containing platinized carbon at a temperature of 60°, the sole product of hydrogenolysis being 2,2-dimethylbutane.



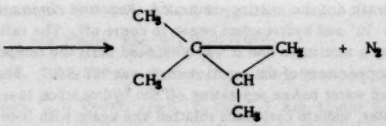
For this investigation we synthesized a large quantity of 1,1,2-trimethylcyclopropane; it is usually prepared by debromination of 2-methyl-2,4-dibromopentane; it was so obtained by Zelinsky and Tselikov [1], Ostling [2], Whitmore and Carney [3], Shortridge and Boord [4], Levina and Gladshtein [5], Bartleson and co-workers [6], and finally in 1952 by Kelso, Greenlee, Derfer and Boord [7]. In the last-mentioned research the synthesis was performed on the large scale and approx. 4 liters of reaction product was fractionated in a column with an efficiency of 135 theoretical plates; it was then found to contain, apart from 1,1,2-trimethylcyclopropane, 2-methylpentane and 2-methylpentenes with the double bond in different positions. The yield of hydrocarbon mixture in this investigation was 60-85%, and about 70% of the mixture consisted of 1,1,2-trimethylcyclopropane.

1,1,2-Trimethylcyclopropane may also be synthesized by Kizhner's method [8]:



mesityl oxide

3,5,5-trimethylpyrazoline



1,1,2-trimethylcyclopropane

This reaction, which gave a good yield of pure 1,1,2-trimethylcyclopropane, was bound up with experimental difficulties since the decomposition temperature of 3,5,5-trimethylpyrazoline (approx. 220°) is above its boiling point (160°). Due to this circumstance the decomposition of the pyrazoline must be carried out in sealed tubes by heating not more than 5 ml of substance for 7-8 hours at 230°.

A recent paper by Petrov [9] gives a short account of the synthesis of 1,1,2-trimethylcyclopropane by the Kizhner reaction whereby the pyrazoline base is decomposed at atmospheric pressure in a catalytic furnace in a flow system in presence of KOH and platinized porcelain at 300°. The author points out that the product of decomposition consists of a mixture of hydrocarbon and undecomposed trimethylpyrazoline which was separated by fractionation. The yield of hydrocarbon is not stated.

We decided to prepare 1,1,2-trimethylcyclopropane by the Kizhner method but without application of pressure using the method proposed by Huang-Minlon [10] for decomposition of alkylidene hydrazines. This method consists in refluxing a mixture of the carbonyl compound, 85% hydrazine hydrate solution, caustic alkali and triethylene glycol at a temperature of 180-220° in a flask. By introducing a few changes into this procedure and using commercial mesityl oxide, from which 3,5,5-trimethylpyrazoline is easily formed, we were able to effect complete decomposition

in eight hours. The yield of hydrocarbon with constant boiling point was 41.7% of the theoretical, reckoned on the pyrazoline base.

Table 1 lists the constants of 1,1,2-trimethylcyclopropane obtained in the above-cited researches and in the present work.

TABLE 1

Authors	B.p. in °C (p in mm mercury)	n_D^{20}	d_4^{20}
Zelinsky and Tselikov [1]	56-57 (750)	1.3848	0.6822
Ostling [2]	59-60 (760)	1.3896	0.6888
Whitmore and Carney [3]	56.5-57.0 (760)	1.3880	0.6967
Ditto [3]	55.5-56.5 (760)	1.3876	0.6941
Lankelma and co-workers [6]	51.7-52.7 (735)	1.3850	0.6853
Levina and Gladshtein [5]	52.0-52.3 (760)	1.3845	0.6861
Kizhner [8]	52.8 (756)	1.3866	0.6949
Kelso, Greenlee, Derfer and Boord [7]	52.55 (760)	1.3864	0.6947
Petrov [9]	53.0	1.3872	0.6927
Present research	52.6 (760)	1.3862	0.6948

EXPERIMENTAL

Preparation of 3,5,5-trimethylpyrazoline. The pyrazoline base was prepared by distilling commercial mesityl oxide (b.p. 127-129°) and an 85% solution of hydrazine hydrate. In a round-bottomed flask fitted with a reflux condenser was placed 96.6 g (3 moles) hydrazine hydrate, and 98.1 g (1 mole) mesityl oxide was slowly run in with stirring. Considerable heat was developed. To the cooled reaction mass was added solid NaOH and the mixture separated into layers. The aqueous layer was removed, the base was dried with solid NaOH, and the unreacted hydrazine hydrate was distilled off; the 3,5,5-trimethylpyrazoline was then distilled from a Favorsky flask to give 70-80 g base boiling at 158-160°. The yield of distilled 3,5,5-trimethylpyrazoline was 60-70% of the theoretical.

Preparation of 1,1,2-trimethylcyclopropane. The synthesis was carried out in a round-bottomed liter flask fitted with a thermometer reaching to the bottom and a glass-packed 30 cm column. The receiver was connected to a spiral trap cooled to −70°. In the flask were placed 78.4 g (1.4 moles) solid KOH, 500 ml triethylene glycol (technical with b.p. 165°/14 mm) and 44.8 g (0.4 mole) distilled pyrazoline base. The mass was gently heated over a burner to drive off a little water (temperature of vapor 100°). When the temperature inside the flask had reached 210°, a sand bath was put underneath and the heating continued. Reaction commenced at 220-235° and the vapor temperature then dropped to 60-70° and hydrocarbon began to come off. The reflux take-off was so adjusted that the vapor temperature was at a minimum and it was continued until the temperature started to rise sharply—this usually occurred when the temperature of the reaction mass was 255-260°. The distillate from the receiver and the trap was diluted with iced water before separating off the hydrocarbon layer. It was washed twice with cooled, dilute hydrochloric acid, water, sodium carbonate solution and again with iced water. The dried hydrocarbon was distilled over metallic sodium in a glass-packed column with an efficiency of 30 theoretical plates to give 14.1 g hydrocarbon boiling at 52.6° (760 mm). The average yield from many experiments was 41.7% of the theoretical reckoned on the 3,5,5-trimethylpyrazoline. Characteristics of the hydrocarbon: d_4^{20} 0.6948; n_D^{20} 1.3862; Found MR 28.43; Calculated for C_6H_{12} MR 27.71; increment of MR 0.72; aniline point of 1,1,2-trimethylcyclopropane 48.3°.

Hydrogenolysis of 1,1,2-trimethylcyclopropane. The catalyst in the form of 10 ml (3.2 g) platinized carbon was charged into a catalysis tube with a diameter of 10 mm, heated in a tubular electric furnace fitted with a resistance of the Heraeus type. The temperature was measured with a chrome-Alumel thermocouple; the hydrocarbon was introduced into the tube through a piston apparatus for uniform proportioning of liquid [11]. The speed of introduction of hydrogen was adjusted so that the volume of gas coming off from the reactor was 1 liter per hour. The catalyzate was collected in a receiver fitted with a trap; the receiver was immersed in a mixture of dry ice and acetone. The catalyst was stabilized by passing through cyclopentane in a hydrogen stream at 300°; after 3 hours the activity of the catalyst for formation of n-pentane was found to be constant. All the subsequent experiments were carried out over this specimen of catalyst. The constants of the paraffinic hydrocarbons which can be obtained by hydrogenolysis of 1,1,2-trimethylcyclopropane are set forth in Table 2.

Results of the experiments are set forth in Table 3.

TABLE 2

Hydrocarbon	B.p. (°C) at 760 mm	n_D^{20}	d_4^{20}
2,2-Dimethylbutane [12]	49.741	1.36876	0.64916
2,3,Dimethylbutane [12]	57.988	1.37495	0.66164
2-Methylpentane [12]	60.271	1.37145	0.65315

TABLE 3

Temp. of exp. in (°C)	Space velocity	n_D^{20} of catalyzate	d_4^{20}
100	0.4	1.3688	0.6492
100	0.4	1.3684	—
60	0.4	1.3684	0.6489
60	0.4	1.3687	—
26	0.4	1.3862	

TABLE 4

Fraction	B.p. in °C at 760 mm	Volume of fraction	n_D^{20}	d_4^{20}
I	49.6-49.8	1.0	1.3687	0.6491
II	49.8	13.0	1.3687	0.6489
III	49.8-80.0	1.0	—	—

The catalyzate from the first four experiments in amount of 16 ml was fractionated in a column containing metallic packing with an efficiency of 30 theoretical plates. 6 ml n-heptane was also introduced into the column. Results of the fractionation are set forth in Table 4.

It is clear from these data that catalytic hydrogenation of 1,1,2-trimethylcyclopropane brings about complete rupture of the three-membered ring even at 60° with formation of 2,2-dimethylbutane.

SUMMARY

1. 1,1,2-Trimethylcyclopropane was synthesized in 41.7% yield by decomposition of 3,5,5-trimethylpyrazoline by Kizhner's procedure except that no pressure was applied.

2. It was established that 1,1,2-trimethylcyclopropane in presence of platinized carbon and hydrogen is completely cleaved at 60° with formation of 2,2-dimethylbutane.

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Received November 25, 1953

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* T.p. = C.B. Translation pagination.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 12. HYDROCONDENSATION OF CARBON MONOXIDE WITH 1-HEXENE

Ya. T. Eidus, N. I. Ershov and E. M. Terentyeva

The catalytic hydrocondensation of carbon monoxide with olefins has been carried out with α-olefins of the aliphatic series containing not more than four carbon atoms in the molecule [1]. Attempts to extend this reaction to tri- and tetra-substituted ethylenes – trimethylethylene and tetramethylethylene– showed [2] that these hydrocarbons only enter to the extent of 5-10% into the reaction of hydrocondensation with carbon monoxide, and are hydrogenated to the extent of 30-50% to isopentane and 2,3-dimethylbutane, respectively. Cyclohexene, which can be regarded as a disubstituted ethylenic hydrocarbon, was only methylated to the extent of 7-10% when we used it in this reaction [3], being transformed into mono- and 1,2-dimethyl- derivatives, while it also partly entered into irreversible catalytic and hydrogenation reactions. It was a matter of interest to establish the reason for the small extent to which cyclohexene entered into the reaction: was it due to the higher molecular weight of this hydrocarbon in comparison with C_2 to C_4 olefins, or to the fact that it is not an α-olefin but a symmetrically disubstituted ethylene? With this objective in the present investigation we have studied the behavior in hydrocondensation with carbon monoxide of 1-hexene, a monosubstituted ethylenic hydrocarbon with a molecular weight differing very slightly from that of cyclohexene.

EXPERIMENTAL

The apparatus and the procedure for the experiments remained the same as in the previous studies [1]. The starting 1-hexene was synthesized by two methods. The first (and simpler) one consisted in dehydration of 1-hexanol (b.p. 156-157°; d_4^{20} 0.8193; n_D^{20} 1.4131) over alumina in a flow system at 350°, with a space velocity of 0.3-0.5 liters/liter/hour in a weak nitrogen stream [4]. After prolonged drying over anhydrous calcium chloride, the hexene was distilled in a column, packed with single metal spirals, with an efficiency of 40 theoretical plates. The 61-66° (754 mm) fraction was again dried for a long period over anhydrous copper sulfate and refractionated in the column. The 63-63.8° (753 mm) fraction was collected; it had d_4^{20} 0.6733; n_D^{20} 1.3882; Found MR 29.50; Calculated for C_6H_{12} MR 29.44. Literature data [5,6]: b.p. 63.7; 63.5° (760 mm), d_4^{20} 0.6733; 0.6747; n_D^{20} 1.3880; 1.3886. About 160 ml 1-hexene was obtained by this method and was used in experiments 226 and 226a. The 1-hexene used in experiments 227 and 228 (amount about 200 ml) was obtained by a second, more complicated, method giving a purer product, free from isomers (2-hexene, 3-hexene, etc.). This second method consisted in the thermal decomposition of hexyl acetate by the method of Van Pelt and Wibaut [7]. In the first step of this synthesis, 1-hexanol is acetylated with a mixture of acetic anhydride, b.p. 137-140° (758 mm), and 10% acetyl chloride, b.p. 50-51° (758 mm) to give hexyl acetate (b.p. 166-171°) in a yield of up to 90% reckoned on the original 1-hexanol. In the second step of the synthesis the acetic ester is decomposed at 460-490° over glass wool in a nitrogen stream at a flow velocity of the ester of 8 drops per minute. The crude reaction product was separated from the acid layer, washed with weak sodium bicarbonate solution and with water, dried over calcined potassium carbonate and distilled from a Favorsky flask. The following 3 fractions were collected:

Fraction I., b.p. up to 75°, yield 77.8%.
Fraction II., b.p. 75-157°, yield 13.7%.
Fraction III., b.p. 157-170°, yield 8.5%.

Fraction I was treated as follows for removal of hexanol from the hexene: It was shaken several times in a separating funnel with concentrated $CaCl_2$ solution, washed with water, dried for a long time over anhydrous $CaCl_2$ and refluxed in a flask over metallic sodium for 2 hours; it was then distilled in a column to 64.5°. The hexene obtained in this way was again distilled in the same column and a fraction was collected in a yield of approx. 50% reckoned on the original 1-hexanol; this fraction had a constant boiling point of 62.7° (743 mm); it had d_4^{20} 0.6734; n_D^{20} 1.3882; Found MR 29.50; Calculated for C_6H_{12} MR 29.44; bromine number found (Kaufmann method) 190.8; calculated 190.7. Fig. 1 shows the curve of fractionation of hexene in the column.

The original 1-hexene was introduced into the glass catalytic tube (diameter 10 mm) from an automatic buret. The experiments were performed at atmospheric pressure and a temperature of 190° in a flow system. The products were collected in two receivers at room temperature and at –80° respectively. The samples of catalyst used were from a single batch.

The experimental data and their evaluation

1. 1-Hexene (without a carrier gas). Apart from investigating the behavior of 1-hexene in hydrocondensation with carbon monoxide, we carried out experiments with 1-hexene along and with a binary mixture of C_6H_{12} and H_2 in similar conditions. Results obtained in an experiment with 1-hexene are set forth in Table 1 (experiment 226a).

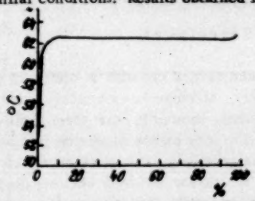

Fig. 1. Curve of fractionation of 1-hexene

Over catalyst 54 (after experiment 228, described below, had been carried out over it, followed by regeneration and purging with nitrogen) was passed 1-hexene for 5 hours with a space velocity of 0.4 liter/liter/hour. From 79 ml hydrocarbon introduced was obtained 75.8 ml (95.9%) liquid catalyzate with the constants d_4^{20} 0.6735 and n_D^{20} 1.3888, only deviating slightly from the constants of the original 1-hexene (see Table 1). Distillation of 60 ml catalyzate from a Favorsky flask resulted in the whole coming over at 62.5-64° (748 mm), indicating recovery of substantially the whole of the original 1-hexene. Nor were any gaseous reaction products obtained.

TABLE 1

Experiment 226-a

Expt. No.	Catalyst No.	Duration of experiment, in hours	Amount of 1-hexene (moles) passed through	Space velocity in liters/liter/hour			Liquid catalyzate obtained		Contraction of gas, in %
				of hexene	of original gas	of C_6H_{12} + gas	in ml	in volume % of original hexene	
226a	54 (regen)	5.0	0.63	0.40	—	92.0	75.8	95.9	—
226	53	8.0	0.47	0.24	101	145	51.9	88.0	61.7
227	53 (regen.)	11.5	0.80	0.29	34	86	92.0	92.0	83.0
228	54	5.0	0.47	0.40	73	144	55.5	92.5	60.0

2. 1-Hexene in a hydrogen stream. Experiment 226 (Table 1) was carried out with 1-hexene in a stream of hydrogen over freshly prepared catalyst 53 (weight of catalyst 20 g, length of layer 40 cm). Hexene was passed through for 8 hours with a space velocity of 0.24 liter/liter/hour. The ratio by volume of 1-hexene to hydrogen in the gas phase was 1 : 3. The contraction of the gas was 61.7%. On the basis of analysis in a Podbielniak column (5.2 liters HTD taken for analysis) and of gas analysis of the separate fractions, the final gas had the composition by volume: 86.3% H_2, 7.0% CH_4, 6% C_2H_4, 0.5% C_2H_6 and 0.2 % C_3H_8. The original hydrogen reacted to the extent of 67.1%. The hydrocarbon gases present in the final gas were products of decomposition of the original hexene and amounted to 3.1 mole-% of the hexene passed through.

From 59 ml starting hexene was obtained 51.9 ml (88%) liquid catalyzate. Heating of the latter to 21° caused 250 ml gas to come off; this gas condensed completely at −80° and had the composition: 13.3% ethylene, 4.4% ethane, 46.7% butylenes and 35.6% butane. Quantitatively this gas represents 1.3 mole-% of the starting hexene. Consequently the gaseous products of hydrogenolysis made up 4.6 % of the total.

After debutanization and drying over anhydrous copper sulfate the catalyzate had d_4^{20} 0.6608; n_D^{20} 1.3786; bromine number 27.0. 42 ml of catalyzate was fractionated in a column with an efficiency of 30 theoretical plates at a pressure of 751 mm. The fractionation curve is shown in Fig. 2.

In Table 2 are detailed the individual cuts, their content by volume in the catalyzate, values of d_4^{20} and n_D^{20}; bromine number and content of unsaturated hydrocarbons.

We see from Fig. 2 and Table 2 that between the limits of 21.0-62.0° about 8.6% (by volume) catalyzate distilled off; between the limits 62.0-69.0° 80% came off. The residue, which was distilled off from a 10 ml Favorsky flask, boiled at 70-150° and represented 8.4% of the catalyzate. Fractions II-IV (Table 2) with a boiling

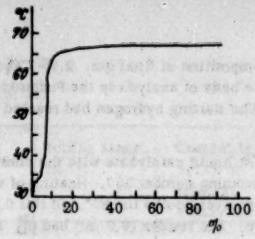

Fig. 2. Curve of fractionation of catalyzate of experiment 226.

range of 33.5-38.5° consisted mainly of n-pentane with a trace of pentene. The largest of these, fraction II, had d_4^{20} 0.6280; n_D^{20} 1.3588, which were very close to the constants of n-pentane [6]: b.p. 36.0°; d_4^{20} 0.6264; n_D^{20} 1.3577. Consequently the liquid product of hydrogenolysis of hexene had a saturated character, which can be explained by the large excess of hydrogen in the original gas. The main bulk of the catalyzate (over 80%) was in fractions VI-IX. As we see from the constants and bromine numbers, these fractions consisted to the extent of 80-90% of hexane (b.p. 68.7°; d_4^{20} 0.6594; n_D^{20} 1.3750 [5]) and to the extent of 10-20% of hexene. On the basis of the data obtained, the starting 1-hexene entered into the reaction to the extent of 84.5% and hydrogenation to hexane took place to the extent of 61.3% (by weight) on the starting 1-hexene and to the extent of 70.8% on the reacted 1-hexene. Higher boiling products accounted for 7.6 and 9.0% respectively, and lower boiling products for 11.7 and 13.7% respectively.

3. 1-Hexene in a mixed stream of carbon monoxide and hydrogen. Two experiments, numbers 227 and 228 (Table 1), were performed with passage of 1-hexene in a stream of a gaseous mixture of carbon monoxide and hydrogen. Experiment 227 was carried out with catalyst 53 after its regeneration and experiment 228 with catalyst 54 (weight of catalyst 15.5 g, length of layer 40 cm) which had previously been used for 5 hours in the hydrocondensation of carbon monoxide with ethylene.

TABLE 2

Experiment 226

Fractions	Boiling range, in °C	Content, in vol-% of original catalyzate	d_4^{20}	n_D^{20}	Bromine number	Amount of unsaturated hydrocarbons, in %	C_n
I	21.0-33.5	0.5	—	—	—	—	C_5
II	33.5-35.5	3.6	0.6280	1.3588	—		C_5
III	35.5-36.0	0.9	—	1.3605	—		C_5
IV	36.0-38.5	0.5	—	—	—		C_5
V	38.5-41.0	0.7	—	—	—		
VI	41.0-62.0	2.4	—	1.3672	—		
VII	62.0-65.5	6.0	0.6590	1.3780	38.1	20	C_6
VIII	65.5-66.5	6.2	0.6602	1.3790	31.4	17	C_6
IX	66.5-67.5	67.5	0.6593	1.3770	18.9	10	C_6
X •							
Residue	(70.0-150)	8.4	0.6846	1.3902	10.4		> C_6
Losses		3.3					
Original catalyzate		100	0.6608 ••	1.3786••	27.0••		

• Less than 0.1 ml came over in the range of 67.6-70.0°.

•• The constants relate to the original catalyzate after taking off fraction I.

Experiment 227. 1-Hexene was passed through for 11.5 hours with a space velocity of 0.29 liters/liter/hour. The space velocity of the gas mixture (11.6 CO; 88.4 H_2) was 34 liters/liter/hour. The composition of the gas phase was 61.0% C_6H_{12}, 4.6% CO, 34.4% H_2. The over-all space velocity (gas and vapor phases) was 86 liters/

liter/hour. The contraction of the H_2-CO gas mixture was 83.0%. Composition of final gas: 2.1% CO_2; 54.0% H_2; 7.1% CO; 12.4% $C_4H_8 + C_3H_6$; 1.4% C_2H_4 and 23.0% C_nH_{2n+2}. On the basis of analysis in the Podbielniak apparatus the $C_1 : C_2 : C_3 : C_4$ ratio in the final gas was roughly 12 : 6 : 1: 12. The starting hydrogen had reacted to the extent of 89.5%, the CO to the extent of 89.8%.

From 100 ml of hexene passed through was obtained 92.0 ml (92%) liquid catalyzate with the constants (after drying over anhydrous copper sulfate): d_4^{20} 0.6753; n_D^{20} 1.3902; bromine number 157. Heating of the dried catalyzate to 28° caused separation of 0.6 ml condensate in the receiver cooled to −80°. Of this 0.6 ml, about 0.4 ml readily changed to gas (about 100 ml) at room temperature. The residue (0.2 ml) had n_D^{20} 1.3750.

The debutanized catalyzate (74 ml) was fractionated in a column with an efficiency of 30 theoretical plates at a pressure of 738 mm. The fractionation curve is shown in Fig. 3.

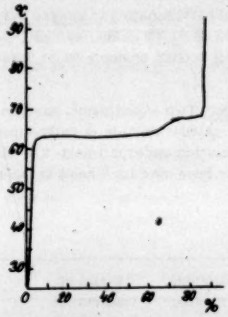

Fig. 3. Curve of fractionation of catalyzate of experiment 227.

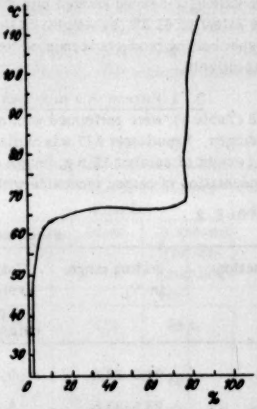

Fig. 4. Curve of fractionation of catalyzate of experiment 228.

In Table 3 are detailed the individual fractions and their constants. As we see from Fig. 3 and Table 3, in the range 28.0-62.5°, 5.4% (by volume) of catalyzate came over; in the range 62.5-70.5° 82% distilled. The residue, which was distilled from a 15 ml Favorsky flask, boiled in the range of 70.5-155° and represented 11.4% of the catalyzate. On the basis of its properties, fraction I was a mixture of pentane and pentene with slight preponderance of the latter; fractions III and IV comprising in all 55.6% of the catalyzate, consisted of nearly pure (95.4-99.6%) 1-hexene. Fractions V and VI comprised a mixture of hexene and hexane in the ratio of 1.7 : 1 and 1: 1.5 respectively.

The data show that in experiment 227 the 1-hexene reacted to the extent of 35.9%. The total yield of hexane was 12.4% (by weight) on the starting and 34.6% on the reacted 1-hexene. The less intense hydrogenation than in experiment 226 may be explained by the lower content of hydrogen in the starting gas. Moreover in experiment 227 the higher boiling products amounted to 13.7% of the starting and 38.2% of the reacted 1-hexene, i.e., more than in experiment 226, which was carried out in the absence of carbon monoxide in the gas phase.

Experiment 228 was conducted with catalyst 54 whose activity had previously been characterized, in a hydrocondensation reaction using 54.8% C_2H_4, 6.8% CO and 38.4% H_2, by a yield of liquid condensate of 554.8 ml/m^3 at a space velocity of the starting gas of 109 liters/liter/hour. After the experiments on hydrocondensation of carbon monoxide with ethylene, hydrogen was passed over the catalyst at 450° for 3 hours; experiment 228 was then started. 1-Hexene was passed through for 5 hours with a space velocity of 0.40 liters/liter/hour. Space velocity of gas mixture (13.6 CO : 86.4 H_2) 73 liters/liter/hour. The composition of the gas-vapor phase was 49.5% C_6H_{12}, 7.0% CO and 43.5% H_2. The over-all space velocity (gas-vapor phase) was 144 liters/liter/hour. Composition of final gas: 1.9% CO_2; 79.8% H_2; 13.7% CO; 0.4% C_4H_8; 4.2% C_2H_4; 0.0% C_nH_{2n+2}. The starting hydrogen reacted to the extent of 63.1%, the carbon monoxide to the extent of 60%. The contraction of the original gas was 60% (Table 1).

TABLE 3

Experiment 227

Fractions	Boiling range, in °C	Content, in vol-% of original catalyzate	d_4^{20}	n_D^{20}	Bromine number	Amount of unsaturated hydrocarbons, in %	C_n
I	28.0-41.0	2.7	0.6386	1.3700	116.3	52	C_5
II	41.0-62.5	2.7	0.6675	1.3858	119.4	63	$C_5 + C_6$
III	62.5-62.6	38.1	0.6721	1.3878	189.7	99.6	C_6
IV	62.6-63.5	17.5	0.6751	1.3875	181.7	95.4	C_6
V	63.5-67.5	17.0	0.6688	1.3865	116.9	62.4	C_6
VI	67.5	9.7	0.6673	1.3850	73.5	39	C_6
VII*	92.5-155.0	11.4	0.7193	1.4110	65.9		$> C_6$
VIII							
Residue and losses		1.9	—	—			$> C_6$
Starting catalyzate		100	0.6753	1.3902	157.0		

* 1.0 ml came over at 67.6-92.5°.

TABLE 4

Experiment 228

Fractions	Boiling limits, in °C	Content, in vol-% of original catalyzate	d_4^{20}	n_D^{20}	Bromine number	Amount of unsaturated hydrocarbons, in %	C_n
I	To 28	1.6	—	—	—	—	
II	28.0-62.0	7.2	0.6520	1.3810	166.7	79	C_5
III	62.0-67.4	68.2	0.6653	1.3848	129.7	68	C_6
IV*	79.5-295.0	19.6	0.7264	1.4140	49.8		$> C_6$
V		2.4	—	—	—		$> C_6$
Residue							
Losses		2.0	—	—	—		
Original catalyzate	28-295	100	0.6988	1.3960	109.2		

* 0.2 ml came over in the range of 67.4-79.5°.

From 60.0 ml starting 1-hexene was obtained 55.5 ml (92.5%) catalyzate, from which (after drying over anhydrous copper sulfate) was isolated, by heating to 28°, 0.8 ml volatile condensate in the receiver cooled to −80°. The liquid catalyzate then had the following properties: d_4^{20} 0.6988; n_D^{20} 1.3960; bromine number 109.2. 50 ml was fractionated in the above-mentioned column (30 theoretical plates) at a pressure of 746 mm. The fractionation curve is shown in Fig. 4. Results of fractionation are set forth in Table 4.

We see from Fig. 4 and Table 4 that in the range of 28.0-62.0 ° (fraction II) 7.2% (by volume) catalyzate comes over; in the range of 62.0-68.8° 68.2% (fraction III) comes over. Fraction IV, which came over nearly completely in the range of 79.5-295°, was distilled from a 25 ml Favorsky flask; it represented 19.6%, and together with fraction V 22.0%, of the condensate. Fraction II, 7.2% of the total, consisted mainly of pentane and pentene with a little hexane and hexene, and contained 79% unsaturated hydrocarbons. Judging by its constants and bromine number, fraction III was a mixture of hexene and hexane in the ratio of approximately 7 : 3. Fraction IV and residue V are products of hydrocondensation of carbon monoxide with 1-hexene. These higher boiling products could not have been formed only from CO and H_2, and they were obtained with participation of the original 1-hexene. This is confirmed by the fact that if all the reacted carbon monoxide had participated only in the Orlov-Fischer-Tropsch reaction, 27 times less product could have been obtained than the total amount of fraction IV and residue V (Table 4). From the data of experiment 228 it follows that 1-hexene entered into the reaction to the extent of 56.7%. 22.6% (by weight) entered into the hydrocondensation reaction with carbon monoxide when reckoned on the original 1-hexene, and 39.8% when reckoned on the reacted 1-hexene. The hexane yield was 20.4 and 36.0% respectively.

Table 5 contains a comparison of the main results obtained in experiments 226, 227 and 228. The table shows that over freshly prepared catalyst at a somewhat low space velocity of 1-hexene (0.24 liters/liter/hour) and with excess of hydrogen in the gas phase ($C_6H_{12} : H_2 = 1 : 3$), i.e. in the conditions favoring hydrogenolysis and reaction of the products with 1-hexene, the latter is hydrogenated to the extent of 61.3% (by weight) to n-hexane; at the same time 7.6% was converted into higher boiling and 11.7% into lower boiling products (experiment 226).

TABLE 5

Expt. No.	Catalyst number	Catalyst	$C_6H_{12} : H_2$ ratio in the gas phase	Amount of CO_2 in %	Yield of high-boiling products, in weight-%		Yield of hexane, in weight-%.	
					on starting 1-hexene	on reacting 1-hexene	on starting 1-hexene	on reacting 1-hexene
226	53	Freshly prepared	1 : 3	0.0	7.6	9.0	61.3	70.8
227	53	Regenerated	1 : 0.56	4.6	13.7	38.2	12.4	34.6
228	54	After hydrocondensation of carbon monoxide with ethylene	1 : 0.88	7.0	22.6	39.8	20.4	36.0

In presence of 4.6 % CO in the gas phase the hydrogenation to hexane proceeded to the extent of 12.4% on the starting hexene and to the extent of 34.6% on the reacted hexene. The yields of higher boiling products were respectively 13.7 and 38.2% (experiment 227); With a content of 7.0% CO in the gas phase the 1-hexene entered into hydrocondensation with carbon monoxide to the extent of 22.6%, representing 39.8% of the reacted hexene. The yield of hexane was 20.4%, of the original and 36.0% of the reacted hexene (experiment 228). A similar effect of CO concentration on hydrocondensation has already been observed many times [1].

Comparison of the data obtained in this research with previous results of experiments with cyclohexene [3] show that 1-hexene enters more easily into hydrocondensation with carbon monoxide than does cyclohexene. This may be due to 1-hexene being an α-olefin whereas cyclohexene is a symmetrically disubstituted ethylenic hydrocarbon. 1-Hexene enters less readily, however, into this reaction than do the gaseous C_2-C_4 α-olefins.

SUMMARY

1. Experiments on the hydrocondensation of carbon monoxide with 1-hexene were carried out.

2. It was shown that in the usual conditions of this reaction, 22% (by weight) of the original 1-hexene enters into this reaction with formation of higher boiling hydrocarbons and about 20% of it is hydrogenated to n-hexane.

3. The yields of hydrocondensation products and of n-hexane on the reacted 1-hexene are respectively 39,8 and 36,0%.

4. The data obtained show that 1-hexene enters into the hydrocondensation reaction with carbon monoxide with greater facility than cyclohexene but less readily than gaseous C_3—C_4 α-olefins.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 13. INFLUENCE OF THE RATIO OF ETHYLENE TO HYDROGEN IN THE ORIGINAL GAS, OF DILUTION WITH NITROGEN AND OF THE SPACE VELOCITY ON THE HYDROCONDENSATION OF CARBON MONOXIDE WITH ETHYLENE

Ya. T. Eidus, K. V. Puzitsky and I. V. Guseva

In previous communications [1, 2, 3] on the hydrocondensation of carbon monoxide with olefins, some data have already been submitted on the influence of the concentration and the ratio of the individual components in the original gas mixture upon the yield of reaction products. It was observed [1] that whereas with a composition of the starting mixture of 1 CO : $2H_2$: $3C_2H_4$ the mean yield of hydrocarbons was 343.3 ml/m^3 or 30.2 ml/liter catalyst per hour, with a composition of 1 CO : $2H_2$: 1.5 C_2H_4 the yield dropped to 195.6 ml/m^3 or 20.0 ml/liter catalyst per hour. It was shown [2] that a special part is played by the CO concentration. With rising CO content of the gas mixture in the range of 0 to 6%, the yield of gas oil steadily increases, followed by light oil and finally by heavy oil. A further fall of yield of the volatile fraction of the reaction products is offset by rise of the yield of heavier fractions, i.e., the degree of polymerization of ethylene increases. In the complete absence of carbon monoxide no polymerization at all of ethylene, propylene and butylene takes place [3]. Maximum velocity of hydrocondensation of propylene and n-butylene with carbon monoxide was observed in presence of 6 - 8% of carbon monoxide in the starting mixture. When 15-20% carbon monoxide is present in the starting gas mixture, its hydrocondensation with propylene and n-butylene is markedly inhibited in comparison with the same reaction with ethylene. The aim of the present research was to investigate the influence on the course of catalytic hydrocondensation of carbon monoxide with ethylene of the following factors: 1) volumetric ratio of ethylene and hydrogen in the starting gas mixture; 2) dilution of the whole of the starting gas mixture with an inert gas (nitrogen); 3) space velocity of the starting gas mixture.

EXPERIMENTAL

The apparatus, procedure for conducting the experiments and purification and method of analysis of the gases did not differ from those previously described [1]. The experiments were performed in a flow system at atmospheric pressure and 190°. All the catalysts used were of identical composition and prepared by the same method.

1. Influence of Volumetric Ratio of Ethylene and Hydrogen in the Starting Mixture

Experiments on the influence of the volumetric ratio of ethylene and hydrogen in the starting mixture of $C_2H_4 - H_2 - CO$ were carried out with catalyst 55 (length of layer 29 cm, volume 25 ml) with a carbon monoxide content of 3 - 6%. Duration of each experiment 5 hours. The experimental results are set forth in Table 1 and in Figs. 1 and 2.

In Table 1, the experiments are not set forth in the order of their performance (which is indicated by the number of the experiments in the first column) but in the order of rising ratio of C_2H_4/H_2 by volume in the original gas (column 4). As we see from Table 1, the content of ethylene varied in the range of 33-68%, that of hydrogen in the range of 11.7-55.2%, and their ratio by volume in the range of 0.61 - 5.81. The space velocity of the whole of the gas mixture in this series of experiments varied to an insignificant extent (94-132 liters/liter · hour). We see from Table 1 and Fig. 1 that when the C_2H_4/H_2 ratio is less than 1 and more than 4, the total yield of hydrocarbons, expressed in ml/m^3 or ml/liter · hour, is considerably lower than when $4 > C_2H_4/H_2 > 1$.

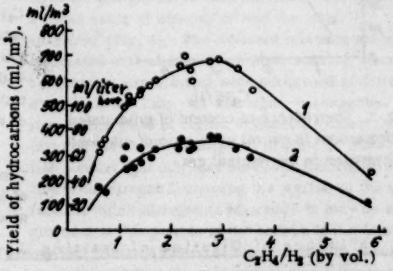


Fig. 1. Influence of ratio by volume of ethylene to hydrogen in starting mixture on yield of hydrocarbons. 1) In ml/m^3; 2) in ml/liter · hour.

TABLE 1

Experiment No.	Amount in original gas, in %		C_2H_4/H_2 ratio by volume	Space velocity in liters/liter·hr.	Contraction, in %	Yield in ml/m³				Yield of T + L + G, in ml/liter·hour	Amount of unsaturateds in gas oil, in %
	C_2H_4	H_2				of heavy oil T	of light oil L	of gas oil G	of T + L + G		
239	33.0	53.7	0.61	118	55.4	79.5	144.5	101.2	325.2	36.0	14.0
237	35.0	55.2	0.63	105	55.7	89.8	122.5	138.7	350.9	34.4	–
240	36.0	50.1	0.72	94	60.2	91.0	127.4	145.6	364.0	32.0	8.0
242	46.0	42.2	1.09	122	64.7	139.8	139.8	223.7	503.3	57.6	–
241	44.5	39.1	1.14	107	65.0	175.6	150.5	183.9	510.0	48.8	–
238	48.0	41.2	1.16	132	65.4	160.6	160.6	224.8	546.0	68.0	–
243	49.0	39.4	1.24	106	65.0	174.9	135.2	206.7	516.8	51.2	–
244	50.5	36.2	1.39	102	68.7	221.4	114.8	213.2	549.4	53.6	28.0
236	52.5	37.4	1.40	127	63.5	173.4	133.3	253.4	560.0	67.2	–
248	54.0	33.7	1.60	109	64.0	234.5	140.6	202.6	577.5	59.2	–
246	55.5	32.6	1.70	115	66.0	232.0	137.7	224.7	594.4	65.6	–
254	61.5	28.7	2.14	104	66.0	203.8	146.7	309.8	660.3	64.8	59.5
245	58.5	26.8	2.18	112	69.2	249.8	151.4	295.3	696.3	73.6	54.0
252	64.0	27.3	2.34	105	63.3	161.0	147.0	338.2	644.1	64.0	65.5
251	64.0	27.2	2.35	111	60.4	150.2	165.2	285.4	600.8	64.0	70.0
247	63.0	22.8	2.76	120	64.0	240.2	155.4	282.6	678.2	76.8	66.0
249	65.0	22.4	2.90	115	64.5	255.0	167.7	269.7	692.4	76.0	71.0
250	70.5	21.7	3.25	108	60.0	124.8	148.1	374.9	647.8	65.6	66.0
255	72.0	20.2	3.56	110	54.3	152.1	159.7	251.0	562.8	59.2	77.0
253	68.0	11.7	5.81	108	36.0	71.4	119.1	39.6	230.1	23.2	–

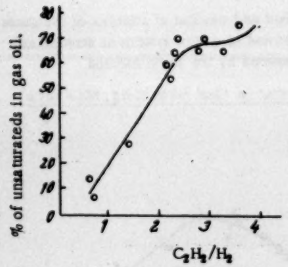


Fig. 2. Dependence of content of unsaturated hydrocarbons in gas oil upon ratio of ethylene to hydrogen in the original gas.

A maximum at a C_2H_4/H_2 ratio of 2.5–3 is observed on the plot of total yield of hydrocarbons versus C_2H_4/H_2 ratio in the starting gas. The highest yield of hydrocarbons is 700 ml/m³ or 70 ml/liter·hour. At a C_2H_4/H_2 ratio of less than 1, the total yield of hydrocarbons falls to 350 ml/m³ or 35 ml/liter·hour. At a C_2H_4/H_2 ratio greater than 4, for example at a ratio of 5.81 (experiment 253), it falls to 230 ml/m³ or 23.2 ml/liter·hour. The yield of light oil hardly changes with change of C_2H_4/H_2 ratio, whereas the yields of heavy oil and gas oil likewise pass through a maximum at a C_2H_4/H_2 ratio of 2 - 3. The rise of the C_2H_4/H_2 ratio is naturally accompanied by an increase of unsaturation of the reaction product. Thus, for example, in the gas oil the content of unsaturated hydrocarbons rises from 8-14 % with a C_2H_4/H_2 ratio of 0.6 - 0.7 to 77 % in the case of a C_2H_4/H_2 ratio of 3.56. The change in unsaturation of gas oil as a function of the C_2H_4/H_2 ratio is plotted in Fig. 2.

Consequently, the data show that a fall in the concentration of hydrogen to a certain limit in comparison with the mixture of 1 CO : $2H_2$: $3C_2H_4$ brings about a rise in yield of the reaction products and an increase in their degree of unsaturation.

2. Influence of Dilution of Starting Gas Mixture with Nitrogen

Experiments in which a study was made of the effect of dilution of the original gas mixture with nitrogen were carried out over the same catalyst 55 before the latter was used for the experiments set forth in Table 1. The duration of each experiment was 5 hours. The original mixture contained 3 - 5 % CO. The experimental results obtained are set forth in Table 2 and plotted in Figs. 3 and 4.

In Table 2 the experiments are set forth in the order of increasing dilution of the starting mixture with nitrogen.

TABLE 2

Experiment No.	Amount in starting mixture		Ratio by volume of C_2H_4/H_2	Space velocity in liters/liter·hour	Concentration in %	Yield in ml/m³				Yield of T + L + G in ml/liter·hour
	of active gases (C_2H_4 + $+H_2+CO$)	N_2				T	L	G	T+L+G	
232	95.4	4.6	1.3	138	65.3	165.7	134.0	243.9	543.6	71.2
235	95.4	4.6	1.2	136	63.0	148.9	161.3	235.8	546.0	70.4
231	72.6	27.4	1.7	131	53.0	218.7	187.5	218.7	624.9	58.1
229	46.4	53.6	1.5	110	32.4	177.4	306.4	16.1	499.9	24.8
234	45.3	54.7	1.8	104	29.2	140.4	280.8	70.2	491.4	22.4
230	37.7	62.3	1.6	144	29.5	192.5	274.0	66.5	533.0	28.8
233	28.8	71.2	1.9	81	24.4	181.0	291.1	18.5	490.6	10.8

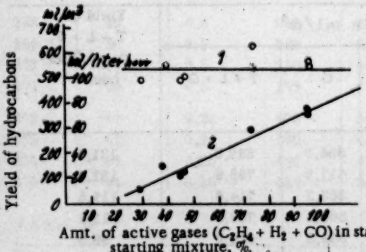


Fig. 3. Yield of hydrocarbons as a function of the dilution of the starting gas with nitrogen: 1 - in ml/m³; 2 - in ml/liter/hour.

Fig. 4. Yield of various fractions of reaction products as a function of the dilution of the initial gas with nitrogen.

The enumerated values of the contraction relate to the whole of the starting mixture, while the space velocity and yields in ml/m³ relate to the active gas (C_2H_4 + H_2 + CO).

Table 2 indicates that the nitrogen content of the mixture varied between 4.6 and 71.2%. We see from Table 1 and Fig. 3, that the total yield of hydrocarbons, expressed as ml/liter·hour, decreases linearly with dilution of the starting mixture with nitrogen. When related to 1 m³ of active gas (C_2H_4 + H_2 + CO), however, the total yield of hydrocarbons does not change appreciably with dilution and has an average value of 530 ml/m³. Similarly, as shown by Fig. 4, the yield of heavy oil in ml/m³ does not depend on the dilution and has a mean value of 180 ml/m³. The yields of light oil and gas oil (in ml/m³), however, vary sharply with dilution; the former in fact rises sharply while the second falls equally sharply with increasing content of nitrogen in the starting mixture to 55%. With further increase of the nitrogen content the yields of light oil and gas oil remain constant – the former at a mean value of 290 ml/m³ and the latter at 40 ml/m³ (Fig. 4). The observed relations are not associated with change of catalyst activity, since consecutive experiments were performed at different dilutions. This – at first sight – unexpected rise of the yield of higher molecular product (light oil) and the corresponding fall in yield of more volatile product (gas oil) may be due to the higher dilution with nitrogen increasing the portion of the surface on which nitrogen is adsorbed. It may be suggested that this portion of the surface is the least active and is characterized by a lower heat of adsorption and desorption. In the absence of nitrogen on this part of the surface the hydrocarbons formed are easily desorbed and do not attain a high molecular weight (gas oil). In the presence of a large amount of nitrogen this part of the surface is covered with nitrogen, and the consequence of this is a drop in the yield of gas oil, which is the more pronounced the greater the amount of nitrogen adsorbed. On the more active portion of the surface of the catalyst the relative concentration of CH_2 groups will be greater than in the experiments without dilution, which results in a rise in the yield of light oil. This explanation, however, calls for additional experimental confirmation.

3. Influence of Space Velocity of the Initial Gas

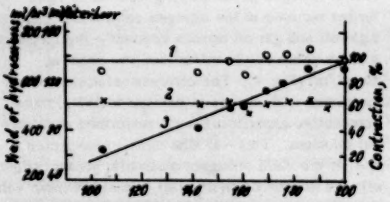
The space velocity may be altered by: 1) changing the linear velocity of the gas at constant volume of catalyst, or 2) changing the volume of the catalyst at constant linear velocity. We effected a change of space velocity by both methods.

a) Change of space velocity with constant volume of catalyst. These experiments were performed on catalysts 56 and 57 (each 18 g, 21 ml, layer length 26 cm). The starting mixture contained 3 - 4 % carbon monoxide and 23 - 30 % hydrogen. The results of the experiments are set forth in Table 3 and plotted in Fig. 5, from which we see that change of space velocity in the range of 105 - 200 liters/liter · hour does not affect the contraction of the gas, which remains at an average value of 62 %, or the total yield of hydrocarbons when expressed in ml/m³, whose mean value was 680 ml/m³. With rising space velocity, however, there is a linear rise in yield, expressed in ml/liter · hour, from 64.0 at a space velocity of 105 liters/liter · hour to 131.4 at 200 liters/liter · hour.

b) Change of space velocity at constant linear velocity. These experiments were carried out with catalysts 58 and 63 (double portions of catalyst, each 32 g), 59 and 62 (ordinary portions of 18 g each), 60 (1/2 portion of 9.7 g) and 61 (1/4 portion of 5 g). Results of experiments with these catalysts are set forth in Table 4 and plotted in Figs. 6 and 7.

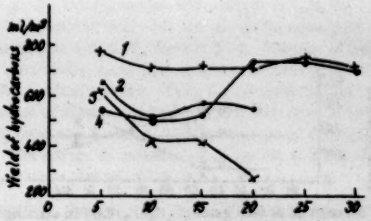
TABLE 3

Experiment No.	Catalyst number	Duration of experiment in hours	Space velocity, in liters/liter · hour	Contraction, in %	Yield, in ml/m³				Yield of T + L + G, in ml/liter · hour
					T	L	G	T + L + G	
262	57	5	200	61.4	149.9	145.0	394.9	689.8	131.4
260	57	25	186	66.9	180.3	153.6	411.9	745.8	131.0
261	57	10	177	66.6	174.1	190.4	350.3	714.8	119.5
259	56	15	170	64.3	167.2	172.6	368.8	708.6	113.0
263	57	10	161	56.9	133.1	162.5	334.3	629.9	99.5
258	56	10	155	64.7	192.9	170.6	322.9	686.4	98.6
257	56	5	143	63.0	189.2	188.2	266.2	643.6	82.7
256	55	5	105	63.3	161.0	147.0	338.2	646.2	64.0



Space velocity in liters/liter · hour

Fig. 5. Influence of space velocity of initial gas at constant catalyst volume on the yield of hydrocarbons: 1) Yield in ml/m³; 2) contraction; 3) yield in ml/liter · hour.



Hours

Fig. 6. Effect of duration of experiment on the dependence of the yield of hydrocarbons on the space velocity of the initial gas: 1) 186 liters/liter · hour, 1 portion; 2) 250 - 300 liters/liter · hour, 1/2 portion; 3) 500 liters/liter · hour, 1/4 portion; 4) 64 liters/liter · hour, 2 portions.

The data of Table 4 and Figs. 6 and 7 show that in experiments with 1/4 portion of catalyst (catalyst 61) at a space velocity of 500 liters/liter · hour the activity of the catalyst falls off with increasing duration of reaction. The yield of hydrocarbons falls from 623.7 to 278.7 ml/m³ or from 284 to 127 ml/liter · hour. In experiments with

TABLE 4

Experiment No.	Catalyst Number	Number of portions of catalyst	Space velocity, in liters/liter·hour	Contraction in %	Yield, in ml/m³				Yield of T+L+G, in ml/liter·hour
					T	L	G	T + L + G	
282	63	2	61	71,2	142,0	142,0	256,0	540,0	30,4
283	63	2	67	68,5	178,1	63,7	356,3	498,1	37,6
284	63	2	68	55,6	161,7	129,8	234,3	525,8	32,4
285	63	2	62	66,3	207,3	129,2	400,4	736,9	41,2
286	63	2	63	66,7	197,3	132,1	410,3	740,3	44,8
276	62	1	185	72,1	176,9	150,0	450,2	777,1	138,0
277	62	1	178	66,2	155,7	205,7	350,4	711,4	121,9
278	62	1	188	63,9	173,7	141,3	401,3	716,3	124,7
279	62	1	176	67,0	192,6	175,1	350,2	717,9	117,1
280	62	1	187	69,4	203,8	128,5	407,8	739,8	131,4
281	62	1	188	64,1	187,3	198,0	337,3	722,6	128,5
268	60	0,5	252	65,2	238,7	173,8	246,4	658,9	152,0
269	60	0,5	298	54,7	169,0	150,7	187,5	507,2	140,0
270	60	0,5	252	50,3	201,3	180,0	194,1	575,4	133,4
271	60	0,5	273	58,6	214,5	167,7	167,7	549,4	137,0
272	61	0,25	500	56,7	220,0	154,0	249,7	623,7	284,0
273	61	0,25	500	48,3	123,7	130,9	160,0	414,0	190,0
274	61	0,25	498	42,1	110,9	147,7	162,5	421,1	190,0
275	61	0,25	527	36,7	73,4	110,2	95,1	278,7	127,0

TABLE 5

Experiment No.	Catalyst Number	Number of portions of catalyst	Space velocity, in liters/liter·hour	Contraction in %	Yield, in ml/m³				Yield of T + L + G, in ml/liter·hour
					T	L	G	T + L + G	
264	58	2	64	65,6	177,4	119,3	331,5	628,2	37,3
266	59	1	124	62,6	264,6	209,0	225,0	698,6	80,0
268	60	0,5	252	65,2	238,7	173,8	246,4	658,9	152,0
272	61	0,25	500	56,7	220,0	154,0	249,7	623,7	284,0

TABLE 6

Experiment No.	Catalyst Number	Number of portions of catalyst	Space velocity in liters/liter·hour	Contraction in %	Yield in ml/m³				Yield of T + L + G in ml/liter·hour
					T	L	G	T+L+G	
267	59	1	142	64,3	195,5	158,8	231,1	585,4	76,8
257	56	1	143	63,0	189,2	188,2	266,2	643,6	82,7
265	58	2	124	61,0	153,7	167,4	381,6	702,7	84,0
266	59	1	124	62,6	264,6	209,0	225,0	696,6	80,0

1/2 and 1 portion of catalyst at space velocities of 250-300 and 186 liters/liter·hour respectively, the yield of hydrocarbons expressed in ml/m³ or ml/liter·hour remains nearly constant. In experiments with a double portion of catalyst at a space velocity of 64 liters/liter·hour, the yield of hydrocarbons expressed in ml/m³ increases with the time, whereas when expressed in ml/liter·hour (product) it remains constant.

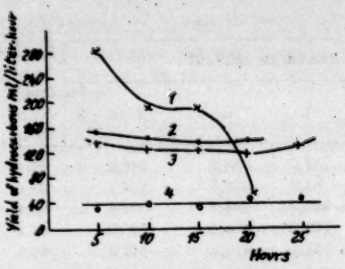


Fig. 7. Effect of duration of experiment on the dependence of the yield of hydrocarbons on the space velocity of the initial gas: 1) 500 liters/liter·hour, 1/4 portion; 2) 250-300 liters/liter·hour, 1/2 portion; 3) 186 liters/liter·hour, 1 portion; 4) 64 liters/liter·hour, 2 portions.

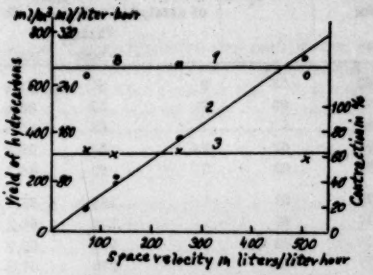


Fig. 8. Effect of space velocity of initial gas at constant linear velocity upon the yield of hydrocarbons: 1) in ml/m³; 2) in ml/liter·hour; 3) contraction.

We may note that in order to compare the results among themselves obtained at different space velocities, the first experiments in order of time in this series were taken. An exception was the double portion of catalyst (catalyst 58) with which the 25-hour experiment number 264 was carried out, and mean values after 25 hours were taken. Results of comparison of the influence of space velocity with changing volume of catalyst while maintaining constant linear velocity are set forth in Table 5 and plotted in Fig. 8.

From Table 5 and Fig. 8 we see that change of space velocity by changing the amount of catalyst has no influence upon the contraction of the gas and upon the total yield of hydrocarbons expressed in ml/m³. The total yield of hydrocarbons expressed in ml/liter·hour, however, increases linearly with the space velocity which was varied in the range of 61-500 liters/liter·hour. In Table 6 for comparison are set forth the data obtained over different catalysts (56 and 59) at one and the same space velocity (142 liters/liter·hour) with one and the same amount of catalyst (experiments 267 and 257) and with different amounts of catalyst (experiments 265 and 266). From Table 6 we see that the results are in fairly good agreement in respect to total yield, expressed as ml/m³ and as ml/liter·hour, in the experiments at one and the same space velocity.

We see from the data obtained that the method of changing the space velocity of the initial gas has little influence upon the reaction course provided that not too little catalyst is taken; too little catalyst shortens the duration of action of the catalyst and leads to a sharp drop in activity in course of time. Increase of space velocity (by either of the methods indicated) in the investigated range does not bring about a change of contraction of the gas or of the total yield of hydrocarbons in ml/m³ but leads to a linear rise of total yield when expressed as ml/liter·hour.

SUMMARY

1. An investigation was made of the influence of the ethylene/hydrogen ratio in the initial gas mixture, of dilution with nitrogen and of the space velocity upon the hydrocondensation of carbon monoxide with ethylene.

2. It was shown that the optimum ethylene/hydrogen ratio in the initial gas is 2.5-3.

3. Dilution of the initial gas mixture with nitrogen does not influence the total yield of hydrocarbons when expressed as ml/m³ but leads to a fall in yield when related to unit time and to unit volume of catalyst. Dilution of the gas with nitrogen up to a certain limit leads to rise of yield (ml/m³) of light oil and a corresponding fall of yield of gas oil.

4. Rise of space velocity in the range of 100-500 liters/liter·hour does not influence the total yield of hydrocarbons expressed as ml/m³ and leads to a linear rise of yield expressed in ml/liter·hour. When using small amounts of catalyst, the latter is quickly deactivated.

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Received, October 30, 1953

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* T.p. = C.B. Translation pagination.

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THERMAL TRANSFORMATIONS OF 1,3-PENTADIENE

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The study of the thermal transformations of individual hydrocarbons is of considerable interest for the understanding of industrial processes for working-up of hydrocarbon raw materials. The literature contains a large number of papers dealing with the thermal decomposition of alkanes and alkenes, whereas the transformations of alkadienes (with exception of butadiene) under the action of high temperature have hardly been studied. Thus, Kennedy and Hetzel [1] studied the reaction of dehydrocyclization of piperylene over various catalysts with the objective of obtaining cyclopentadiene; they showed that the maximum yield of this hydrocarbon is approximately 9% at 600° and a pressure of 10 - 30 mm mercury. The composition of the other products of transformation of piperylene was not studied. Frank, Emmick and Johnson [2] obtained two fractions on passing trans-piperylene at 600° through a vertical pyrex glas tube filled with glass packing:

Fraction I, b.p. 38-41.5°; yield 5%
Fraction II, b.p. 43.2°; yield 52%

The second fraction contained, apart from the original trans-piperylene, 45% of cis-piperylene.

From publications on the thermal transformations of hydrocarbons [3, 4, 5, 6] it is known that alkanes do not tend to form cyclic systems in the conditions of thermal treatment, whereas alkenes form cyclic compounds in appreciable quantity. In this research we studied the thermal transformations of 1,3-pentadiene at various temperatures in a flow system.

EXPERIMENTAL

The piperylene used in the investigation had the following characteristics: b.p. 42-42.5° (760 mm); n_D^{20} 1.4315; d_4^{20} 0.6830. Literature data: b.p. 42.4-42.6°; n_D^{20} 1.4309; d_4^{20} 0.6803 [7].

Reaction with maleic anhydride [2] enabled establishment of the ratio of stereoisomeric forms in the starting material; the latter proved to be a mixture of 53% cis- and 47% trans-isomers. The original 1,3-pentadiene was subjected to thermal treatment in a quartz tube with an internal diameter of 18 mm, heated by an electric furnace and filled with crushed quartz glass. Substitution of porcelain for the quartz did not alter the character of the pyrolytic transformations. A temperature of 600° was used; the rate of passage of the diene was 0.3 liter per liter contact material per hour. The condensate was collected in two traps arranged in series and cooled with a mixture of acetone and solid carbon dioxide.

The gaseous products of pyrolysis were analyzed in an Orsat-Lunge apparatus and by low-temperature fractionation in vacuum. The liquid products of the reaction were investigated by means of rectification, chromatographic resolution and bromination of individual fractions. The solid products of reaction (coke) were characterized by determination of their elemental composition.

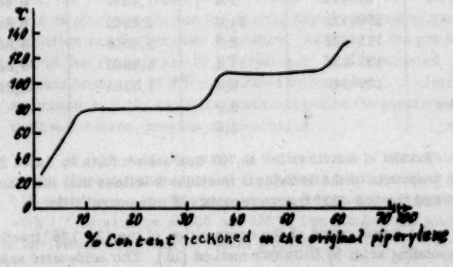

Fig. 1. Curve of fractionation of condensate from pyrolysis of piperylene.

Several preliminary experiments were carried out in which the reproducibility of the results was determined, the yields of condensates were established, and the content of cyclopentadiene and of partly sulfonatable condensate boiling up to 140° was found. The results of the experiments showed that the condensates contain up to 1% cyclopentadiene and 15% of substances

which are taken up by 82 % sulfuric acid. Cyclopentadiene was determined by the colorimetric method described by Afanasyev [8]. These experiments were followed by others in which the composition of the condensates was studied in more detail. Below are set forth the data of one typical run at 600° in which from 68 g pentadiene was obtained 50 g (74 % of the original) pyrolyzate with a dark-brown color. This condensate was fractionated in a column with an efficiency of 27 theoretical plates. Results of fractionation are set forth in Table 1 and plotted in Fig. 1.

TABLE 1

Results of Fractionation of Condensate Obtained by Thermal Treatment of Piperylene

Fractions	B.p.(°C)	Yield of fractions in %	n_D^{20}	Fractions	B.p.(°C)	Yield of fractions in %	n_D^{20}
I	26 - 29	–	1,3950	VIII	78 - 90	26,4	1,4995
II	29 - 34	1,4	1,4095	IX	90 - 108	2,0	1,4950
III	34 - 35	1,6	1,4025	X	108 - 110	18,0	1,4968
IV	35 - 37	0,7	1,4090	XI	110 - 135	0,8	1,4930
V	37 - 39	0,3	1,4173	XII	135 - 140	7,2	1,4958
VI	39 - 45	2,8	1,4370	Residue		36,0	–
VII	45 - 78	0,8	1,4680	Losses		2,0	–

It follows from the data of Table 1 and Fig. 1 that pentadiene is transformed into a complex mixture of hydrocarbons containing a considerable proportion of substances of high molecular weight. It is noteworthy that the pyrolyzate contains a large amount of aromatic hydrocarbons; for their identification a portion of the combined condensate from several experiments was resolved into an aromatic and an aliphatic fraction by the method of chromatographic adsorption [9]. 42,5 g condensate taken for chromatographic analysis gave 37 g (87%) aromatic hydrocarbons with n_D^{20} 1,5015, slightly contaminated with saturateds, and 4 g (10 %) unsaturated hydrocarbons with n_D^{20} 1,4490. Fractionation established the absence of unsaturated hydrocarbons higher than C_8, but there was considerable contamination with aromatics. The aromatic hydrocarbons were fractionated in a column with an efficiency of 27 theoretical plates.

TABLE 2

Results of Fractionation of Aromatic Portion of Condensate from Thermal Transformations of Piperylene

Fractions	B.p.(in °C)	Yield in %	d_4^{20}	n_D^{20}	Molecular refraction MR	
					Found	Calculated
I	38-79	1,3	1,3905	–	–	–
II	79-80	34,0	1,4998	0,8782	26,17	26,31
III	80-109	2,4	1,4980	0,8665	–	–
IV	109-111	31,0	1,4962	0,8658	31,11	30,93
V	111-135	3,5	1,4940	0,8651	–	–
VI	135-136	11,3	1,4960	0,8652	35,79	35,54
VII	136-140	6,9	1,5085	0,8995	–	–
Residue		8,0	–	–		
Losses		1,6				

Results of fractionation at 760 mm are set forth in Table 2 and plotted in Fig. 2. From an inspection of the properties of the individual fractions it follows that the fraction with b.p. 79-80° consists of benzene (34 %) and the 109-110° fraction consists of toluene (31,0 %).

For investigation of the composition of the 135-136° fraction, 2 g of the fraction was oxidized to the corresponding acids by Ullmann's method [10]. The acids were separated and analyzed by the procedure described by Moldavsky, Kamusher and Kobylskaya [11]. Among the products of oxidation were found 0,40 g benzoic acid with m.p. 121°, 0,08 g orthophthalic acid with m.p. 190° (in sealed capillary), 0,33 g isophthalic acid and 1,10 g terephthalic acid with melting points of 63 and 138° for the respective dimethyl esters. Calculations on the basis of these results show that the 135-140° fraction contains 25 % ethylbenzene, 5 % o-xylene, 26 % m-xylene and 44 % p-xylene.

At the conclusion of the fractionation of the aromatic part of the pyrolyzate, a solid with the odor of

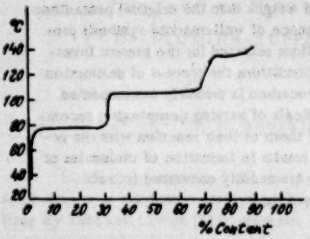

Fig. 2. Results of fractionation of aromatic portion of condensate after thermal treatment of piperylene.

naphthalene crystallized on the walls of the condenser. After recrystallization this substance (0,17 g) was dissolved in a little ethanol and poured into an alcoholic solution of an equimolar amount (0,3 g) picric acid. The resultant yellow needles were identified from the melting point (148°) as the monomolecular compound of naphthalene and picric acid. The literature [12] gives 149.5° as the m.p.

For analysis of the low-boiling portion of the pyrolyzate, the combined 29 - 37° fraction from several experiments (2,5 g) was brominated at 0°. The crystalline bromides (0,2 g) were separated from the liquid bromides (2,7 g). The solid tetrabromides were twice recrystallized from ethanol; they melted at 113-114°, which is the m.p. of 1,3-pentadiene tetrabromide. The liquid bromides were fractionated at reduced pressure (18 mm) to give fractions with b.p. 70-100°, 0,3 g; n_D^{20} 1,5340 (the greater portion boiled at 70-80°) and with b.p. 100-160° (predominantly 150-160°), 2,0 g, n_D^{20} 1,5880.

Analysis of fraction with b.p. 100-160°:

Found %: C 15,93; H 2,17; Br 81,9

$C_5H_8Br_4$. Calculated %: C 15,49; H 2,08; Br 82,43

On the basis of the analytical results we may conclude that the 70-100° fraction contains mainly the dibromo derivatives of C_5 alkenes, while the 100-160° fraction contains isoprene tetrabromide, reported in the literature to have b.p. 157-159° (12,5-13,5 mm) [13].

Consequently, the volatile fraction of the condensate evidently contains (apart from piperylene) isoprene, pentenes and cyclopentadiene (main bulk in the 39-45° fraction)*. After passing 50 ml piperylene over the catalyst, 0,3 g coke had settled on the catalyst or the equivalent of 1% by weight of the original pentadiene. Analysis of two samples of coke (I – C 94,24% and H 5,76%; II – C 94,92% and H 5,08%) showed that it corresponds in composition to a condensed aromatic compound with the general formula $C_n H_{2n-18}$.

TABLE 3

Composition of gaseous products of thermal transformations of piperylene at various temperatures

Composition of gas	Temp. in °C		
	500	550	600
Hydrogen	27	22	23
Unsaturated C_2–C_4 hydrocarbons	3	12	23
Saturated C_1–C_4 hydrocarbons	70	66	54

It was observed that in subsequent experiments carried out in the same conditions but without regeneration of the catalyst, the yield of liquid product fell to 70-66%. This fall in yield of pyrolyzate is due to the coke deposit promoting gas formation and further coke formation. Analysis of the gas revealed that it contained 32,6% hydrogen, 54,6% saturated hydrocarbons, and 22,8% unsaturated hydrocarbons. A closer examination of the saturated portion revealed the presence of methane, ethane, propane and isobutane.

A study was also made of the influence of temperature on the character and extent of the thermal transformations of 1,3-pentadiene. For this purpose experiments were carried out with 1,3-pentadiene at 500 and 550°. The condensates were analyzed by the same methods as before. Results of analyses are set forth in Tables 3 and 4.

It follows from the data of Tables 3 and 4 that rise of temperature from 500 to 600° increases the extent of transformations of pentadiene: the amount of aromatic hydrocarbons and resins increases considerably while the content of low-boiling hydrocarbons decreases appreciably. Rise of temperature causes a significant increase in the content of unsaturated hydrocarbons in the gaseous products.

In conclusion it is necessary to mention that thermal treatment of 1,3-pentadiene in a flow system leads

* The total content of cyclopentadiene in the condensate, as indicated above, was determined in a broad cut boiling up to 140°.

TABLE 4

Composition of liquid products of thermal transformations of piperylene at various temperatures

Composition of liquid products	Temp. in °C		
	500	550	600
Unsaturated hydrocarbons with b.p. 26-39°	22	22	4
Unsaturated hydrocarbons with b.p. 39-45°	50	18	4
Aromatic hydrocarbons	15	28	54
Resin	13	32	38

to formation of a complex mixture of hydrocarbons both richer and poorer in hydrogen than the original hydrocarbon. The presence in the condensates of hydrocarbons higher in molecular weight than the original pentadiene points to the occurrence of well-marked synthesis processes in the conditions selected for the present investigation. In these conditions the process of destruction of the original hydrocarbon is probably accompanied by formation of radicals of varying complexity; recombination of some of them or their reaction with the original hydrocarbon results in formation of molecules of hydrocarbons which are readily converted into six-membered cyclic systems.

SUMMARY

1. An investigation was made of the thermal transformations of 1,3-pentadiene (piperylene) in a flow system at 600° in a quartz tube filled with crushed quartz glass.

2. In the specified conditions 1,3-pentadiene forms a complex mixture of hydrocarbons of various classes: gaseous (methane, ethane, propane, isobutane, alkenes), liquid (isoprene, pentenes, cyclopentadiene, benzene, toluene, xylenes) and solid (naphthalene, and condensed systems with the general formula C_nH_{2n-12}).

3. The yield of cyclopentadiene does not exceed 1% reckoned on the original 1,3-pentadiene.

4. Formation of a considerable amount of aromatic hydrocarbons must be attributed to condensation reactions of dienes.

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Received July 9, 1953

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CONTACT CATALYTIC ALKYLATION OF BENZENE IN PRESENCE OF ALUMINA-SUPPORTED ZINC CHLORIDE UNDER CONDITIONS OF HIGH PRESSURE

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Insufficient attention has been given in the literature to problems of utilization of metallic halides on a solid support as alkylation catalysts. The methylation of benzene in the vapor phase was effected for the first time by Kutz and Corson [1] in presence of aluminum chloride adsorbed on activated carbon. The application of aluminum chloride as a vapor phase alkylation catalyst is mentioned in patents [2, 3]. In 1945 Schmerling and Ipatieff [4] took out a patent on the methylation of aromatic hydrocarbons in presence of zinc chloride on alumina. At 250-350°, according to the authors, the yield of toluene is 22%, and that of xylenes 25%.

Zinc chloride has been used as a catalyst for alkylation of the aromatic nucleus with alkyl chlorides and alcohols by Kuchkarev and Tsukervanik [5] who showed that condensation of benzene with n-butyl and isopropyl alcohols at 220-230° in an autoclave gives monoalkylbenzenes in a yield of 75-80% of the theoretical, calculated on the alcohol. Condensation of benzene with ethyl alcohol only takes place at 300° to form ethylbenzene in a yield of 36% of the theoretical.

In the present investigation we studied the catalytic alkylation of benzene with diethyl ether, ethylene and isopropyl alcohol in presence of alumina-supported zinc chloride. The reaction was performed in a flow system at high pressure (10 to 60 atm) and temperatures of 150-400° at various molar ratios of benzene to the alkylating agent. Alkylation of benzene with ethylene was carried out in contact with alumina and with alumina-supported zinc chloride (15 and 30% $ZnCl_2$). The experiments showed that in favorable conditions alumina does not catalyze the alkylation of benzene with ethylene. Zinc chloride supported on alumina in the amount of 15 and 30 wt-% proved an active catalyst for this reaction.

In the conditions that we established (see p. 785) the yield of broad ethylbenzene fraction with b.p. 120-140° was 16% of the theoretical reckoned on the benzene used.

In the alkylation of benzene with isopropyl alcohol the highest yields of isopropylbenzene were obtained at temperatures of 300 to 350° and pressures of 20 to 40 atm. and with a molar benzene/isopropyl alcohol ratio in the range of 4:1 to 6:1. In these conditions the yield of broad isopropylbenzene fraction (b.p. 145-160°) was 78-80% of the theoretical and that of pure isopropylbenzene (b.p. 152-153°) was 63.3% reckoned on the isopropyl alcohol taken. In the reactions which we studied, the best results were obtained by alkylation of benzene with isopropyl alcohol.

EXPERIMENTAL

Catalytic alkylation of benzene with diethyl ether, ethylene and isopropyl alcohol was carried out in a flow system. In all experiments a mixture of benzene (39 g, i.e., 0.5 mole) and alkylating agent was charged into the reactor with a space velocity of 0.45 at temperatures of 150 to 400°. The catalyzate was fractionated from a small flask with a tall Vigreux column (h = 0.5 m). In the tables are included the most typical results of the experiments. As a rule 2-3 experiments were carried out in each set of identical conditions.

Catalytic Alkylation of Benzene with Diethyl Ether

Results of the experiments on alkylation of benzene with diethyl ether are set forth in Tables 1 and 2. The influence of the benzene/diethyl ether molar ratio is plotted in curves 1 and 2 of Fig. 1. Curve 1 shows that the yield of ethylbenzene, reckoned on the ether taken, falls with increasing amount of the latter, while the yield with reference to benzene (curve 2) at first rises slowly to a maximum and then gradually falls. The benzene/ether molar ratio in the range of 4.5:1 to 6:1 may be considered the optimum.

It was established in the experiments that the most suitable conditions for alkylation of benzene with diethyl ether in contact with alumina-supported zinc chloride at high pressure are: temperature of 300 to 350°,

pressure of 20 atm, and a benzene/ether molar ratio in the range of 4.5 : 1 to 6 : 1. In these conditions the yield of broad ethylbenzene fraction with b.p. 120-140° is 13-14% of the theoretical reckoned on the benzene taken, or 74-86% reckoned on the reacted benzene.

TABLE 1

Influence of the temperature upon the catalytic alkylation of benzene with diethyl ether (Pressure 20 atm; benzene/ether ratio = 6 : 1)

Expt. No.	Temp. in deg C.	Weight of catalyzate, in g	Results of fractionation of catalyzate (amount of fraction in g)						
			up to 85°	85-120°	120 - 140°			140-200°	Residue in g
					in g	Yield in %			
						on the benzene	on the ether		
9	250	40.0	26.0	2.5	6.2	11.5	43.5	2.3	1.5
4	300	40.5	29.0	1.5	7.0	13.2	41.2	1.0	0.5
7	350	36.0	22.0	2.5	7.5	14.1	43.0	1.5	1.6
8	400	41.0	29.0	1.5	7.0	13.2	41.2	1.0	1.0

TABLE 2

Influence of pressure on the catalytic alkylation of benzene with diethyl ether (Temperature 300°, benzene/ether molar ratio = 6 : 1)

Expt. No.	Pressure in atmospheres	Weight of catalyzate, in g	Results of fractionation of catalyzate (amount of fraction in g)				
			up to 85°	85-120°	120-140°	140-200°	Residue in g
4	20	40.5	29.0	1.5	7.0	1.0	0.5
12	30	37.0	20.0	2.0	7.1	2.9	4.0
13	40	37.5	20.0	1.5	6.5	3.1	4.5
14	60	38.0	21.6	2.0	6.0	4.5	5.1

Contact catalytic alkylation of benzene with ethylene

A mixture of 40% ethylene and 60% nitrogen was used for the alkylation of benzene with ethylene with the aim of reducing the yields of polyalkylbenzenes. The reaction was carried out at pressures of 20 to 40 atm and temperatures of 225 to 350° with various amounts of ethylene. Results of experiments on alkylation of benzene with the above-mentioned mixture in contact with various samples of catalysts are set forth in Table 3.

TABLE 3

Dependence of yields of alkylbenzenes on the nature of the catalyst in the alkylation of benzene with ethylene

Expt. No.	Catalyst	Temp. of expt., in deg C.	Molar ratio of benzene to ethylene	Catalyzate obtained in g	Yield of alkyl fraction in %
7	Zinc chloride on alumina (30% $ZnCl_2$)	300	1 : 1	39.0	30.7
18	Zinc chloride on alumina (15% $ZnCl_2$)	300	1 : 1	35.0	32.0
4	Alumina	300	1 : 2	35.0	none
5	Alumina	370	1 : 1	36.0	none

We see from Table 3 that alumina does not catalyze the alkylation of benzene with ethylene. Zinc chloride (15 and 30 wt-%) supported on alumina proved an active catalyst for this reaction.

In the following experiments a study was made of the influence of temperature (Table 4, experiment 7,8,9), of pressure (Table 4, experiments 6 and 11), and of the molar ratio of benzene to ethylene (Table 4, experiments 14, 15, 17) on the yield of the ethylbenzene fraction.

TABLE 4

Alkylation of benzene in contact with alumina-supported zinc chloride

Expt. No.	Temperature (°C)	Pressure, in atm.	Molar ratio of benzene to ethylene	Weight of catalyzate (in g)	Results of fractionation of catalyzate (weight of fraction in g)					
					up to 85°	85-120°	120-140°		140-200°	residue, in g
							in g	yield on benzene (in %)		
8	225	20	1 : 1	38.0	29.5	1.3	3.7	6.9	1.5	1.8
7	300	20	1 : 1	39.0	24.0	1.6	6.5	12.0	2.4	2.5
9	350	20	1: 1	39.0	27.0	1.5	5.0	9.5	3.5	2.0
6	300	20	2 : 1	36.0	25.0	1.5	5.0	9.5	2.0	1.5
11	300	40	2 : 1	48.0	18.0	5.0	8.5	16.0	3.0	11.5
14	300	40	3 : 1	41.0	24.0	1.5	6.5	12.0	3.2	5.0
15	300	40	2 : 1	41.0	17.0	3.0	7.5	14.0	5.0	7.0
17	300	40	1 : 2	35.0	16.6	2.0	7.5	14.0	4.2	4.5
18*	300	Atmosph.	1 : 2	38.5	37.0	0.5	—	—	—	0.5

* The experiment was carried out at atmospheric pressure in a flow system.

The optimum conditions for alkylation of benzene with ethylene in contact with alumina-supported zinc chloride are: temperature 300 deg, pressure 40 atm, and molar ratio of benzene to ethylene of 2 : 1. The catalyzate obtained in these conditions contains 50% alkylbenzenes including 18.5% broad ethylbenzene fraction (b.p. 120-140°), representing 16% of the theoretical yield reckoned on the benzene taken.

The 85-120° and the 120-140° fractions from all the experiments were combined, treated with sulfuric acid to eliminate the small content of unsaturateds, washed with water, dried with calcium chloride and distilled over sodium in a column with an efficiency of 25 theoretical plates. They contained 58% ethylbenzene with b.p. 134-136°; n_D^{20} 1.4956 and d_4^{20} 0.8677, and 2% toluene with b.p. 109-112°; n_D^{20} 1.4960 and d_4^{20} 0.8670. The fractionation curve of these fractions is plotted in Fig. 2. The 109-112° fraction was oxidized by Ullmann's method to give benzoic acid which after sublimation melted at 121°. On the basis of the fractionation data the yield of pure ethylblenzene in the most successful experiment was 14.7% of the theoretical.

The combined 140-190° fractions of all the catalyzates were treated with sulfuric acid, washed with water, dried with calcium chloride and distilled over sodium in a small column. From 22 g of this broad cut was isolated a 10 g fraction with b.p. 175-186°; its constants (n_D^{20} 1.4965; d_4^{20} 0.8703) show that in the main it consists of diethylbenzenes.* Oxidation of this fraction by Ullmann's method [7] gave a mixture of phthalic acids. Separation of this mixture by the method described by Moldavsky and co-workers [8] indicated that the investigated fraction contained 15.4% o-diethylbenzene, 46.2% m-diethylbenzene and 38.1% p-diethylbenzene. The combined residues from the fractionation of the catalysts from all the experiments boiled in the range of 190-300° and was evidently a mixture of polyalkylbenzenes.

* Boiling points: o-diethylbenzene, 183.3°; m-diethylbenzene, 181.25°; p-diethylbenzene, 183.6°

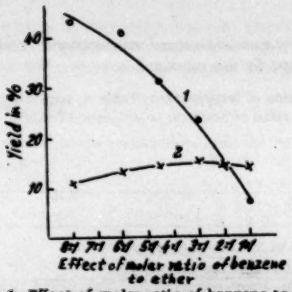

Fig. 1. Effect of molar ratio of benzene to diethyl ether on yield of the broad ethylbenzene fraction (b.p. 120-140°) at 300° and 20 atm. 1) Yield calculated on ether taken; 2) yield calculated on benzene taken.

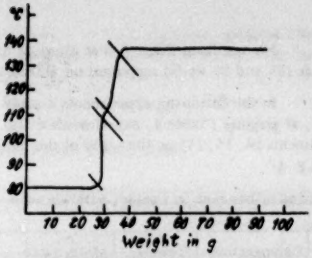

Fig. 2. Curve of fractionation of combined fractions with b.p. 85-120° and 120-140°

Alkylation of benzene with isopropyl alcohol

During alkylation with isopropyl alcohol a study was made of the influence of temperature, pressure and molar ratio of benzene to isopropyl alcohol. The influence of pressure was studied at 250° and a molar benzene/alcohol ratio of 4 : 1 (these conditions proved to be the optimum when carrying out this reaction at atmospheric pressure [9]). Results of the experiments are set forth in Table 5.

Table 5 shows that increase of pressure to above 20 atm has an insignificant effect upon this reaction; in the pressure range of 40 to 60 atm the yield of isopropylbenzene remains constant.

TABLE 5

Influence of pressure on yield of the isopropylbenzene fraction (Temperature 250°, molar ratio of benzene to alcohol = 4 : 1)

Pressure in atm.	Weight of catalyzate, in g	Results of fractionation of catalyzate (amount of fraction in g)					
		up to 85°	85-145°	145-160°			Residue in g
				in g	Yield in %		
					on benzene	on alcohol	
10	40.0	28.0	0.5	10.0	16.6	66.6	0.3
20	40.5	27.8	0.8	10.5	17.5	70.0	0.4
40	41.0	27.5	0.5	11.0	18.3	73.3	0.5
60	40.0	26.7	0.5	11.0	18.3	73.3	1.5

The temperature effect was examined at a benzene/alcohol molar ratio of 4 : 1 and at a pressure of 40 atm (Table 6).

According to the data of Table 6 the maximum yield of isopropylbenzene is obtained at temperatures between 300 and 350°.

The influence of the molar ratio of benzene to isopropyl alcohol was studied at 300° and 20 atm. The results of these experiments are plotted in curves 1 and 2 of Fig. 3, from which we see than an increase in the amount of alcohol in the reaction mixture leads to a drop in yield of the isopropylbenzene fraction with b.p. 145-160° when reckoned on the original isopropyl alcohol, and to a rise in yield of this fraction when calculated on the benzene introduced.

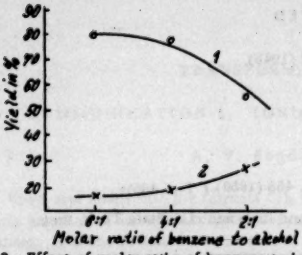

Fig. 3. Effect of molar ratio of benzene to isopropyl alcohol on the yield of the isopropylbenzene fraction with b.p. 145-160°; 1- yield calculated on the isopropyl alcohol introduced; 2- yield calculated on the benzene introduced.

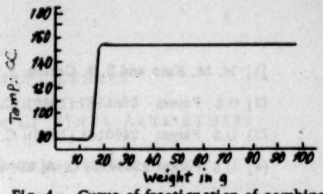

Fig. 4. Curve of fractionation of combined fractions with b.p. 85 145° and 145-160°.

Fractionation of the combined alkylbenzene fractions with b.p. 85-145° and 145-160° in a column with an efficiency of 25 theoretical plates gave 78% pure isopropylbenzene with b.p. 152-153°; n_D^{18} 1.4921 and d_4^{20} 0.8585 (Fig. 4). On the basis of the pure hydrocarbon the maximum yield of isopropylbenzene (b.p. 152-153°) is 66.3% of the isopropyl alcohol introduced.

TABLE 6

Influence of temperature on yield of isopropylbenzene fraction in the catalytic alkylation of benzene with isopropyl alcohol (Pressure 40 atm., molar ratio of benzene to alcohol = 4 : 1)

Expt. No.	Temperature (°C)	Weight of catalyzate (in g)	Results of fractionation of catalyzate (amount of fraction in g)					
			up to 85°	85-145°	145-160°			Residue (in g)
					in g	Yield, in %		
						on benzene	on alcohol	
4	150	38.0	33.1	0.4	3.0	5.0	20.0	0.6
1	200	39.0	30.5	0.3	7.5	12.5	50.0	0.3
2	250	41.0	27.5	0.5	11.0	18.3	73.3	0.4
3	300	40.3	22.5	0.8	11.7	19.5	78.0	0.5
5	350	43.0	29.5	0.8	11.5	19.0	76.6	0.6

SUMMARY

1. Conditions were established for alkylation of benzene with diethyl ether, ethyl and isopropyl alcohols in contact with alumina-supported zinc chloride in the vapor phase at elevated pressure.

2. In the conditions established for the alkylation of benzene with diethyl ether the yield of broad-cut ethylbenzene fraction with b.p. 120-140° is 13-14% of the theoretical reckoned on the benzene taken and 74-86% on the reacted benzene.

3. Alkylation of benzene with ethylene gave ethylbenzene (b.p. 134-136°) in a yield of 14.7% of the theoretical reckoned on the benzene introduced into the reaction. Other reaction products were toluene and a mixture of diethylbenzenes consisting of 15.4% meta-isomer, 46.2% meta-isomer, and 38.1% para-isomer.

4. Alkylation of benzene with isopropyl alcohol in the selected conditions gave a 66.3% yield of isopropylbenzene (b.p. 152-153°) calculated on the alcohol taken.

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Received November 24, 1953

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* T.p. = Consultants Bureau Translation pagination.

TRANSFORMATIONS OF VINYL ARYL ETHERS

COMMUNICATION 1. IONIC POLYMERIZATION OF VINYL ARYL ETHERS

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Vinyl aryl ethers with the formula $CH_2 = CH - OAr -$ have been little studied. Development of methods for their preparation and utilization involves a study of the processes of activation of the molecules of these substances. It is known that the activation of chemical compounds may proceed under the influence of substances capable of decomposing into ions or free radicals. On this basis the ability of an organic compound to react under the influence of ionic catalysts or radical initiators determines its reactivity to a considerable extent.

Investigation of various transformations and properties of vinyl aryl ethers permits clarification of the reactivity of these compounds and comparison of the reactivity with that of vinyl alkyl ethers. We commenced such an investigation with reference to the hydrolysis and hydrohalogenation of vinyl phenyl ether [1,2], to the addition of alcohols, and to the breakdown of its α-halo derivatives [3]. A study of these reactions showed that the reactivity of vinyl aryl ethers in presence of ionic catalysts is lower than that of vinyl alkyl ethers. For the purpose of fuller investigation of the transformations of vinyl aryl ethers we thought it expedient to study their polymerization and copolymerization both by ionic and radical mechanisms. These investigations throw adequate light on the chemical activation of molecules of vinyl aryl ethers and pave the way to synthesis of new derivatives of this series.

The experiments have shown that the reactivity of vinyl aryl ethers in polymerization processes under the influence of ionic catalysts is even more seriously inhibited than in the above-mentioned transformations.

The present communication is devoted to the ionic polymerization of vinyl aryl ethers, which is being studied by us in close connection with other transformations of vinyl ethers. Whereas the ionic polymerization of vinyl alkyl ethers has been adequately dealt with in the literature [4,5], the question of the polymerization of vinyl aryl ethers has up to now remained unclarified. Apart from a patent [6] and the exploratory study of Losev and co-workers [7], no investigations in this field have been reported.

As we have shown [1,2], hydrolysis and hydrohalogenation of vinyl phenyl ether in presence of ionic catalysts proceed with considerably greater difficulty than the corresponding reactions of vinyl alkyl ethers. This is because the activity of the ethereal oxygen is considerably weakened by the presence of the benzene ring, so that the formation (1), isomerization (2) and dissociation (3) of the oxonium complex proceed at a lower velocity:

$$CH_2 = CH - OAr + HX \longrightarrow CH_2 = CH - \underset{\displaystyle HX}{OAr}. \qquad (1)$$

$$CH_2 = CH - \underset{\displaystyle HX}{OAr} \rightleftharpoons CH_3 - CHX - OAr. \qquad (2)$$

$$CH_3 - CHX - OAr \longrightarrow CH_3 - \overset{+}{C}H - OAr + \overline{X}. \qquad (3)$$

The complex cation (3) formed during isomerization may give rise to transformations by a cationic mechanism. Reactions of addition, polymerization and copolymerization proceeding according to this mechanism can be represented by schemes (4) and (5):

$$CH_3 - \overset{+}{C}H - OAr + ROH \longrightarrow CH_3 - CH\begin{matrix}\diagup OAr \\ \diagdown OAr\end{matrix} + \overset{+}{H} \qquad (4)$$

$$CH_3 - \overset{+}{C}H - OAr + CH_2 = CH - OR \longrightarrow CH_3 - \underset{\displaystyle OAr}{CH} - CH_2 - \underset{\displaystyle OR}{\overset{+}{C}H} \qquad (5)$$

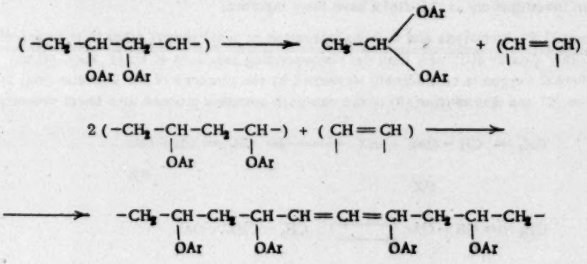
where R = Alk, Ar.

Compounds selected for study of copolymerization of vinyl aryl ethers were vinyl phenyl ether $CH_2=CH-OC_6H_5$ and vinyl p-tert-butylphenyl ether $CH_2=CH-OC_6H_4(C_4H_9\text{-tert})$. The catalysts used were aprotonic agents ($FeCl_3$, $AlCl_3$, and BF_3 etherate) either in the pure form or in the form of solutions of various concentrations and in various solvents. By varying the catalyst, the temperature, and the polymerization procedure, polymers of various molecular weights were obtained, ranging from oils to solids. Experiments were carried out in the range between 15° and the boiling point of the ether. Since the complex formed dissociates at different temperatures with different catalysts, the polymerization temperature is an important factor in this process. The most active catalyst in all cases was BF_3, probably due to the complex of vinyl ether with BF_3 having the lowest dissociation temperature.

Application of the method of purification of polymers of vinyl alkyl ethers to polyvinyl aryl ethers did not give satisfactory results. A method is proposed for purification and fractionation with the objective of obtaining pure products.

Vinyl aryl ethers differ from vinyl alkyl ethers in giving polymers which contain complex mixtures of homologous polymers. The presence of low-molecular fractions suggests the possibility of polymerization of, for example, vinyl phenyl ether taking place not by a chain mechanism but by a stepwise mechanism. In fact, the polymers of vinyl phenyl ether which were isolated included solid high-molecular fractions corresponding to the hexamer and higher. In this connection it was observed that with falling temperature of the experiment the yield of high-molecular fraction increased, and conversely. Thus the lowest yield of high-molecular fraction was obtained in experiments at the boiling point of the ether at atmospheric pressure, whereas on boiling in vacuum the yield of high-molecular fraction increased threefold.

For the purpose of a more detailed examination of the low-molecular fraction of polyvinyl phenyl ether, the latter was fractionated in vacuum and also subjected to molecular distillation. The objective was to isolate the individual compounds present in the original polymer or products of their transformation and breakdown. Vacuum fractionation of the low-molecular fraction of polyvinyl phenyl ether showed that in these conditions the polymer is decomposed with formation of diphenyl acetal and a resinous residue having a higher molecular weight than the original polymer. The rise of molecular weight of the residue may be caused by condensation of molecules of polymer and addition to them of the acetylenic bridge resulting from formation of diphenyl acetal. This possibility is supported by the increased carbon content of the residue. The proposed mechanism may be represented by the following hypothetical scheme.



(6)

Formation of similar acetylenic residues has been repeatedly observed in our laboratory with various substances and is probably characteristic of many derivatives of vinyl ethers. It was observed in the decomposition of α-haloethylaryl ethers [3] as well as after ionic transformations of the vinyl ether of β-phenylaminoethanol [8]. The acetylenic residue $-C\equiv C-$ which is formed on breakdown of the original product is a bridge which can consolidate the remaining molecules of the original substance.

Molecular fractionation of the low-molecular portion of polyvinyl phenyl ether gave a fraction which, judging by the data obtained, was a dimer. It is interesting that in this case, just as in that of vacuum fractionation, a condensed residue was obtained, but since the conditions of molecular fractionation excluded breakdown according to scheme (4), the carbon content of the non-distillable residue corresponded to the pure vinyl phenyl ether.

Polymers of vinyl p-tert-butylphenyl ether are solid, transparent and nearly colorless products, soluble in most organic solvents except methanol and ethanol. They also dissolve in mixtures of these alcohols with benzene and dioxan. This last circumstance makes impossible the separation of these polymers into fractions by the method of precipitation with alcohols. All the isolated polymers and their fractions were characterized by determination of the molecular weight, viscosity, solubility and elemental composition. The data are set forth in Tables 1 and 2.

TABLE 1

Characteristics of polymers of vinyl aryl ethers and their fractions

Serial number	Experimental conditions	Catalyst and its amount	Polymer isolated				Fraction I				Fraction II	
			% yield	outward appearance	mol. wt.	viscosity in centipoises	% yield	mol. wt.	viscosity in centipoises	m.p. (°C)	mol. wt.	viscosity in centipoises
1	Without heating 24 hours	1.5% dry $FeCl_3$	73.0	clear, viscous	383.5	0.6774	15.5	740.0	——	73-74	354.0	—
2	ditto	1.5% dry $AlCl_3$	80.2	Dark, m.p. 40-42	405.3	0.6781	11.0	1000.0	0.6836	61-63	349.0	0.7004
3	ditto	0.1% $BF_3(C_2H_5)_2O$	68.0	Clear, viscous	373.5	0.7969	—	——	——	—	—	—
4	At the boil under atm. pressure 1 hr.	0.012% FeCl (solution in dioxan)	70.5	Dark viscous	351.0	0.6787	6.3	680.0	——	—	333.0	0.6797
5	At the boil in vacuum 2.5 hours	0.12% $FeCl_3$ (solution in dioxan)	94.0	Clear viscous	349.0	0.6752	15.0	965.2	0.6936	86-88	286.0	0.6764
6	At the boil in vacuum 1 hour	0.02% $BF_3(C_2H_5)_2O$ (solution in dioxan)	86.0	Clear, viscous	355.0	0.6960	7.8	756.0	0.7042	76-78	317.0	—

TABLE 2

Solubility of polymers of vinyl aryl ethers and their fractions*

Solvent	Polymer of vinyl phenyl ether	Fr. I of polymer of vinylphenyl ether	Fr. II of polymer of vinylphenyl ether	Polymer of vinyl-p-tert-butylphenyl ether
Acetone	+	X	+	+
Benzene	+	+	+	+
Toluene	+	+	+	+
Dioxan	+	+	+	+
Ether	+	X	+	+
Butyl alcohol	−	−	−	+
Ethyl alcohol	−	−	−	−
Methyl alcohol	−	−	−	−
Ethyl acetate	+	+	+	+
Vinyl phenyl ether	+	+	+	+
Vinyl butyl ether	+	+	+	+
Acetic acid	X	−	+	+
Gasoline (straight run)	−	−	X	+
Sunflower, olive oil	+	−	+	+
Ethylene glycol monoethyl ether	X	−	+	+

* + soluble X not completely soluble; − insoluble

EXPERIMENTAL *

The starting vinyl aryl ethers had the following constants: vinyl phenyl ether: b.p. 155-156°; n_D^{20} 1.5225; d_4^{20} 0.9772; vinyl p-tert-butylphenyl ether: b.p. 219-220°; n_D^{20} 1.5102; d_4^{20} 0.9332.

Polymerization of vinyl phenyl ether

Without heating in the presence of $FeCl_3$, $AlCl_3$ or BF_3 etherate. An ampoule containing 10 g vinyl phenyl ether and 0.15 g dry catalyst or 1 ml 8% solution of $FeCl_3$ in dioxan or 0.5 ml 10% solution of BF_3 etherate in diethyl ether was left at 15-18°. Marked rise of viscosity was observed after 30 min. for BF_3 and after 3 hours for $FeCl_3$. When the viscosity had ceased to change, the polymer was extracted with a solvent or decanted and subjected to purification, dehydration and fractionation (details below). Yields and characteristics of the polymers and their fractions, obtained by this method, are set forth in Table 1.

With boiling under atmospheric pressure, with $FeCl_3$ as catalyst. 30 g vinyl phenyl ether was placed in a three-necked flask fitted with stirrer, thermometer, dropping funnel and reflux condenser. At 155-156° (boiling point) dropwise addition was made in the course of 30 min. of 0.1 ml 4 % solution of $FeCl_3$ in dioxan; during this operation the temperature in the flask gradually rose to 187°, after which it began to fall. In one-half hour after the catalyst had been added, stirring was stopped and the viscous, dark polymer was removed and subjected to purification and fractionation.

Found %: C 79.82; 79.70; H 6.90; 6.82
Calculated %: C 79.97 H 6.72 C_8H_8O.

* Senior Assistant M. Š. Egorova assisted in the experimental work.

Yield of polymer 70.5%. Characteristics of the polymer and fractions are given in Table 1.

With boiling of the ether in vacuum, in presence of $FeCl_3$ Polymerization in vacuum was effected in a three-necked flask fitted with a reflux condenser and a Vigreux column, a thermometer, a capillary reaching to the bottom, and a trap placed between the condenser and the pump and cooled to −20°. The flask was heated on a petroleum jelly bath.

To 30 g vinyl phenyl ether at 56° (22 mm) (b.p. of the ether) was added dropwise in the course of 10 min. 0.9 ml of 4% solution of $FeCl_3$ in dioxan. After 2.5 hours' heating of the ether to 62-72° (20 mm), the colored but transparent polymer was worked up in the usual way to give 26.4 g very viscous, clear polymer.

Found %: C 80.40; 80.53; H 6.76; 6.91
Calculated %: C 79.97; H 6.72 C_8H_8O.

Yield of polymer 94.0%. Characteristics of the polymer and of its fractions are given in Table 1.

With boiling of the ether in vacuum, in presence of BF_3 etherate. To 50 g vinyl phenyl ether at 59° (17 mm) was added 3 drops of 15% solution of BF_3 etherate in dioxan. After 40 min. the temperature started to rise gradually to 92° (16 mm) in the course of 30 min. At the end of this period, a stream of ammonia gas was passed through the polymer to neutralize the catalyst, and the very viscous, colorless, transparent polymer was worked up in the usual way to give 43 g polymer (86.0% of the theoretical).

Found %: C 79.93; 79.87; H 6.66; 6.59
Calculated %: C 79.97; H 6.72 C_8H_8O.

Purification of the polymers of vinyl aryl ethers

The crude polymer discharged from the reaction flask was treated (in the usual steam distillation apparatus) with steam. In this way 400-500 ml (for 50 g polymer) aqueous distillate was taken off, which contained unpolymerized vinyl aryl ether, traces of phenol and acetaldehyde. After separation from the aqueous layer, the polymer was a clear, viscous product which was dehydrated by dissolving in benzene to form a 30% solution. The solution was filtered through a paper filter and the benzene was distilled off from the transparent solution at 40-50 mm. The residue was dried in a vacuum-desiccator at 10 mm and 50° to constant weight. The polymer obtained in this manner was a transparent, clear product.

Fractionation and examination of fractions of polyvinyl phenyl ether

Fractionation of polyvinyl phenyl ether prepared with BF_3 in vacuum. 10.25 g dry polyvinyl phenyl ether was dissolved in 40 g benzene (dioxan could also be used). To each 60 ml methanol placed in a 200 ml conical flask was added 5 ml of the polymer solution; on shaking quickly, a white, clotty precipitate came down which was separated by filtration through a glass filter. After washing with methanol and drying in a vacuum-desiccator to constant weight, the separated fraction (I) was a white, light powder (0.8 g). The solvent was driven off from the filtrate and the residue dried in vacuum to form a clear, transparent, viscous polymer (9.5 g) (fraction II). The characteristics are given in Table 1.

Examination of the low-molecular fraction II. a) Fractionation at 14 mm. 12.0 g fraction II was fractionated in vacuum to give a fraction with b.p. 98-130° (14 mm); weight 2.3 g; residue 8.8 g.

From the obtained fraction was separated 0.4 g (3.3%) crystalline phenol and 1.7 g (14.2%) diphenyl acetal with the constants: b.p. 150-151° (16 mm); n_D^{20} 1.5585; d_4^{20} 1.0870.

The undistillable residue was a brittle, amber-colored resin with m.p. 45-47°, odorless, soluble in diethyl ether, vinyl phenyl ether, dioxan and benzene; insoluble in gasoline and alcohols.

Found M: 473.0; 457.0
Calculated M: 506.59 $(C_8H_8O)_4\ C_2H_2$.
Found %: C 81.23; 81.36; H 6.99; 7.11
Calculated %: C 80.70; H 6.80 $(C_8H_8O)_4\ C_2H_2$.

b) Fractionation in high vacuum. 57 g of fraction II of polyvinyl phenyl ether was fractionated in a molecular still. The following fractions were collected:

Fraction I, b.p. to 100° ($5-10^{-3}$ mm); 11.2 g
Fraction II, b.p. 100-140° ($5-10^{-3}$ mm); 18.0 g.
Fraction III, b.p. 140-168° ($3-10^{-3}$ mm); 2.0 g ; Residue 19.0 g.

For fraction I was found M: 224.0, 230.4. Fraction II was a faintly colored, viscous product, free from odor, soluble in the majority of organic solvents except ethanol.

Found M: 233.0; 240.0
Calculated M: 240.28 $(C_8H_8O)_2$.
Found %: C 79.47; 79.70; H 6.75; 6.99
Calculated %: C 79.97; H 6.72 C_8H_8O.

For fraction III was found M: 266.8; 266.3. The residue was a brittle solid with m.p. 45-50°, soluble in ether, acetone, benzene, dioxan, vinyl ethers, partly soluble in acetic acid and insoluble in gasoline and alcohols.

Found %: C 79.91; 79.96; H 6.94; 6.89
Calculated %: C 79.97; H 6.72 C_8H_8O.
Found M: 470.6; 484.4;
Calculated M: 481.12 $(C_8H_8O)_4$.

Polymerization of vinyl p-tert-butylphenyl ether

Without heating, in presence of dry $FeCl_3$. 5 g vinyl p-tert-butylphenyl ether and 0.05 g (1%) $FeCl_3$ were left at room temperature for 24 hours. 4.6 g (92% of the theoretical) solid, clear product was isolated with m. p. 42-44°.

Found %: C 81.21; 81.37; H 8.80; 8.99
Calculated %: C 81.77; H 9.15 $C_{12}H_{16}O$.
Found M: 471.20
Calculated M: 528.75 $(C_{12}H_{16}O)_3$.

Without heating, in presence of BF_3 etherate. 5.2 g vinyl p-tert-butylphenyl ether and 3 drops of 16% solution of BF_3 etherate in dioxan [0.2% $BF_3(C_2H_5)_2O$] was left for 24 hours. 4.3 g (80% of the theoretical) clear, solid polymer was isolated; this possessed properties similar to the polymer isolated in the previous experiment.

With boiling in vacuum in presence of BF_3 etherate. To 30 g vinyl p-tert-butylphenyl ether at the boil (94° and 8 mm) in the course of 30 min. was added 6 drops of 16% solution of BF_3 etherate in dioxan [0.065% $BF_3(C_2H_5)_2O$]. During the next hour the temperature in the flask rose to 124° at 8 mm (at a bath temperature of 115°) and then began to fall. The ether changed into a clear, green-colored viscous mass which solidified on cooling. 26.0 g (86.7%) of clear, solid polymer with m.p. 40-41° was obtained after purification and drying.

Found %: C 81.62; 81.62; H 9.18; 9.23.
Calculated %: C 81.77; H 9.15 $C_{12}H_{16}O$.
Found M: 452.1; 457.5
Calculated M: 528.75 $(C_{12}H_{16}O)_3$.

The viscosity of this polymer was 0.7082 centipoise. The solubility of the polymer of vinyl p-tert-butylphenyl ether is given in Table 2.

SUMMARY

1. The catalytic action of $FeCl_3$, $AlCl_3$ and $BF_3(C_2H_5)_2O$ on vinyl aryl ethers was studied. It was established that catalytic action on the vinyl aryl ether is developed at temperatures between 15° and the boiling point of the ether.

2. Conditions were established for preparation of polymers of vinyl phenyl and vinyl p-tert-butylphenyl ethers which permitted quantitative yields of polymers.

3. Methods are proposed for purification and separation of polyvinyl phenyl ethers which enable isolation of products of various degrees of polymerization. The characteristics of the isolated polymers and their fractions are given.

4. A study was made of the behavior of the low-molecular fractions of polymers of vinyl phenyl ether in the conditions of vacuum distillation. A probable mechanism of their breakdown in these conditions is advanced.

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Received June 20, 1953

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TRANSFORMATIONS OF VINYL ARYL ETHERS

COMMUNICATION 2. RADICAL POLYMERIZATION AND COPOLYMERIZATION OF VINYL ARYL ETHERS

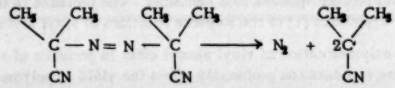
M. F. Shostakovsky and A. V. Bogdanova

The investigation of the conditions of polymerization of vinyl aryl ethers by a radical mechanism is a continuation of the study of the reactivity of compounds of this series. For this purpose we also studied the copolymerization of vinyl aryl ethers with vinyl alkyl ethers. Joint polymerization of these compounds is a valuable synthetic method of preparation of high-molecular substances with diverse properties on the one hand, and offers the possibility of comparing the reactivity of the original monomers on the other hand.

In the preceding communication [1] we described the polymerization of vinyl aryl ethers under the influence of ionic catalysts and compared the behavior of these compounds with that of vinyl alkyl ethers. Both the polymerization reactions and other ionic transformations of vinyl aryl ethers [2,3] show that the activation of their molecules is inhibited. Inhibition of activation of vinyl aryl ethers under the influence of ionic catalysts suggests an analogy with substances which are activated with the help of radical initiators. This prompted us to attempt to activate the molecules of vinyl aryl ethers with an agent which easily breaks down into free radicals. In the literature on the polymerization of vinyl ethers [4] the possibility of such a polymerization is denied in principle, and consequently vinyl ethers have been classed among the compounds which polymerize solely in presence of ionic catalysts.

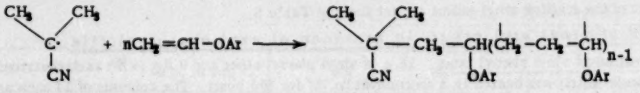
It is known [5,6] that vinyl alkyl ethers can be made to copolymerize with substances which polymerize under the action of peroxide initiators. Such a phenomenon was also observed in the case of α-methylstyrene [7]. But none of these data relate to vinyl aryl ethers.

In the present communication we submit the results of an investigation of reactions of polymerization and copolymerization of vinyl phenyl and vinyl p-tert-butylphenyl ethers with vinyl ethyl and vinyl butyl ethers. The initiator selected for starting free radical reactions was azoisobutyronitrile, which breaks down into free radicals according to the scheme:



(1)

The radicals formed are also activators of the start of various processes and, in particular, of polymerization and copolymerization according to the scheme:



(2)

where Ar = C_6H_5; C_6H_4 (C_4H_9 tert.).

The fact that polymers and copolymers are formed supports the above-mentioned suggestion that vinyl aryl ethers can be activated by radical initiators. This fact, together with the previously noted inhibition of ionic reactions of vinyl aryl ethers, justifies the conclusion that in their degree of reactivity these compounds (II) occupy a position intermediate, as it were, between vinyl esters (I) and vinyl alkyl ethers (III):

$CH_2=CH-OCOAlk$	$CH_2=CH-OAr$	$CH_2=CH-OAlk$
(I)	(II)	(III)

Polymers of vinyl aryl ethers obtained in presence of azoisobutyronitrile (Table 1) are solid, transparent, faint-yellow products, soluble in the majority of organic solvents except alcohols. Purification, drying and fractionation of the polymers were effected by the procedure previously described for polyvinyl aryl ethers prepared

by ionic polymerization [1]. The composition and properties of the isolated products were determined by elementary analysis, molecular weight determinations, and examination of solubility in various solvents (Table 2). Table 2 includes for comparison the solubilities of polymers of vinyl ethyl and vinyl butyl ethers found by Gladyshevsky.

TABLE 1

Polymerization of vinyl phenyl ether in presence of azoisobutyronitrile

Amount of catalyst, in %	Experimental temperature, in °C	Duration, in hours	Yield of polymer, in %	Found				Formula	Calculated			
				mol. wt.	C %	H %	N %		mol. wt.	C %	H %	N %
1.0	60	280	7.2	787.0	78.07	7.18	—	$C_8H_8O_5C_8H_{12}N_2$	736.9	78.23	7.11	—
4.0	60	100	14.0	805.0	78.80	6.93	2.5	$C_8H_8O_6C_4H_6N$	788.9	79.16	6.90	1.78
4.0	75	100	21.6	894.0	79.06	7.15	1.8	$C_8H_8O_7C_4H_6N$	909.0	79.27	6.88	1.53
Fr. I from expt. 1		—	17.1	1833.0	79.18	6.87	1.5	$C_8H_8O_{14}C_8H_{12}N_2$	1818.2	79.27	6.87	1.53

Copolymers of vinyl aryl ethers differ from their polymers in being soluble in alcohols and gasoline, in being viscous products and in having, as a rule, a higher molecular weight; the latter is characteristic of all polyvinyl alkyl ethers. The polymer of vinyl para-tert-butylphenyl ether is soluble in ethyl alcohol and partly soluble in methyl alcohol. The composition of the isolated copolymers shows that copolymerization of vinyl aryl and vinyl alkyl ethers in presence of azoisobutyronitrile is accompanied by formation of polymeric products containing a considerably higher percentage of vinyl aryl ethers than of vinyl alkyl ethers, notwithstanding that in all cases the amount of vinyl aryl ether taken was less than or equal to that of the vinyl alkyl ether. This circumstance enables comparison of the reactivity of vinyl ethers.

In the course of investigation of the isolated polymers, it was established that more high-molecular fractions can be separated from polyvinyl phenyl ether. A fraction as isolated, for example, which corresponded to a tetradecamer, while the low-molecular fraction corresponded to a pentamer. The presence in the prepared polymers of various polymer - homologs supports the hypothesis [1] of the stepwise reactions of vinyl aryl ethers.

As was shown by the experiments on polymerization of vinyl phenyl ether in presence of azoisobutyronitrile the amount of the latter and the temperature and duration profoundly affect the yield of polymer (see Table 1). Intensification of all these factors caused only a small rise in molecular weight of the polymers. In all experiments on polymerization and copolymerization the unreacted portions of the original monomers were recovered unchanged.

EXPERIMENTAL*

The constants of the starting vinyl ethers are set forth in Table 3.

Polymerization of vinyl aryl ethers in presence of azoisobutyronitrile.

1. Polymerization of vinyl phenyl ether. 15 g of vinyl phenyl ether and 0.6 g (4 %) azoisobutyronitrile were sealed into an ampoule which was heated in a thermostat to 75° for 100 hours. The contents of 14 such ampoules, which were heated simultaneously (210 g vinyl phenyl ether), were fractionated with steam. 170 g vinyl phenyl ether (b.p. 155-156 °; n_D^{20} 1.5230) was recovered. In the residue was a light-yellow solid which was freed from catalyst by twice treating with boiling methyl alcohol; it was then dried to constant weight in a vacuum-desiccator. Yield 45.4g (21.6% of the theoretical) of polymer of vinyl phenyl ether with m.p. 48-49° (in capillary). Viscosity of polymer 0.6971 centipoise.

Found %: C 79.06; 79.09: H 7.15; 7.12; N 1.57; 2.0
Calculated %: C 79.27; H 6.88 N 1.53 $(C_8H_8O)_7C_4H_6N$.
Found M: 903.7; 885.0
Calculated M: 909.0 $(C_8H_8O)_7C_4H_6N$.

Fractionation of polymer. Separation into fractions of the prepared polymer was performed by the previously described procedure [1]. From 9.7 g polymer of vinyl phenyl ether was isolated:

*Senior technician M.S. Egorova took part in the experimental work.

TABLE 2

Solubility of polymers and copolymers of vinyl aryl ethers prepared in presence of azoisobutyronitrile *

Solvent	Polymer of vinyl phenyl ether	Copolymer of vinyl phenyl ether with vinyl ethyl ether	Polymer of vinyl ethyl ether.	Copolymer of vinyl phenyl ether with vinyl butyl ether	Polymer of vinyl butyl ether	Copolymer of vinyl p-tert-butyl-phenyl ether with vinyl butyl ether	Polymer of vinyl p-tert-butyl phenyl ether.
Acetone	+	+	+	+	+	+	+
Benzene	+	+	+	+	+	+	+
Toluene	+	+	+	+	+	+	+
Dioxane	+	+	+	+	+	+	+
Diethyl ether	+	+	+	+	+	+	+
Butyl alcohol	−	X	+	+	+	+	+
Ethyl alcohol	−	X	+	−	+	+	X
Methyl alcohol	−	−	−	−	−	X	X
Ethyl acetate	+	+	+	+	+	+	+
Vinyl phenyl ether	+	+	+	+	+	+	+
Vinyl butyl ether	+	+	+	+	+	+	+
Acetic acid	+	+	+	+	+	+	+
Straight-run gasoline	−	−	+	+	+	+	+
Ethylene glycol monoethyl ether	+	X	−	+	−	+	+

* + soluble; X partly soluble; − insoluble

TABLE 3

Ether	b.p. in deg C.	n_D^{20}	d_4^{20}
Vinyl phenyl	155-156	1.5225	0.9770
Vinyl p-tert-butylphenyl	219-220	1.5102	0.9332
Vinyl butyl	93-93.5	1.4020	0.7790
Vinyl ethyl	36-36.5	1.3780	0.7530

For Fraction II, m.p. 44-45°

Found %: N 2.13 2.19;
Calculated %: N 2.10 $(C_8H_8O)_6C_4H_6N$.

Fr. I., 1.9 g (17.1 % of theoretical).
Fr. II., 7.3 g (75.2% of theoretical).

Both fractions were solid, transparent, brittle products.

For Fraction I, m.p. 69-70°.

Found %: C 79.27; 79.09
H 6.86; 6.88; N 1.4; 1.6
$(C_8H_8O)_{14}C_9H_{11}N_3$.
Calculated %: C 79.27;
H 6.87; N 1.53
Found M: 1766.0; 1900.0;
$(C_8H_8O)_{14}C_9H_{11}N_3$. Calculated M: 1818.2

Found M: 653.6; 647.9

Calculated M: 668.9 ($(C_8H_9O)_8C_4H_6N$.

2. Polymerization of vinyl p-tert-butylphenyl ether. From 75 g vinyl p-tert-butylphenyl ether and 3.0 g (4%) azoisobutyronitrile, in the conditions of the above-described experiment, were isolated 58.5 g unreacted monomer with b.p. 109-110° (15 mm); n_D^{20} 1.5090 and 13.5 g (17.6% yield) polymer with m.p. 48-49°. Viscosity of polymer 0.7036 centipoises.

Found %: C 79.69; 79.91; H 8.83; 9.13; N 1.82; 1.97

Calculated %: C 80.49; H 9.12; N 2.34 ($C_{12}H_{16}O)_8C_4H_6N$.

Found M: 572.3; 580.2

Calculated M: 596.83 ($(C_{12}H_{16}O)_8C_4H_6N$.

Copolymerization of vinyl aryl ethers with vinyl alkyl ethers

1. Copolymerization of vinyl phenyl ether with vinyl butyl ether. A mixture of 10 g (0.08 mole) vinyl phenyl ether, 10 g (0.1 mole) vinyl butyl ether and 0.4 g (2%) azoisobutyronitrile was sealed into an ampoule and heated to 65-70° for 100 hours. From 10 such ampoules (200 g starting ethers) was recovered 170.0 g of mixture of monomers, and 10 g (9.7%) of a light-yellow, transparent, very viscous polymer was isolated.

Found %: C 77.11; 77.25; H 8.35; 8.28; N 1.38; 1.32

Found M: 743.0; 735.2

The viscosity of the polymer was 0.7190 centipoise. The copolymer contains: 60.5 (mole-%) vinyl phenyl ether and 39.5% vinyl butyl ether.

2. Copolymerization of vinyl phenyl ether with vinyl ethyl ether. In the conditions of the preceding experiment, 100.0 g (0.83 mole) vinyl phenyl ether, 72.0 g (1.0 mole) vinyl ethyl ether and 3.4 g (2%) azoisobutyronitrile were heated in ampoules to give 142.0 g monomers and 16.1 g (9.3% of the theoretical) of a clear, nearly solid polymeric product.

Found %: C 77.48; 77.40; H 7.92; 7.76; N 1.54; 1.74

Found M: 718.7; 724.1

Viscosity of copolymer 0.7038 centipoise. The copolymer contains: 71.65 mole-% vinyl phenyl ether and 28.35 mole-% vinyl ethyl ether.

3. Copolymerization of vinyl p-tert-butylphenyl ether with vinyl butyl ether. A mixture of 16.4 g (0.1 mole) vinyl p-tert-butylphenyl ether, 10 g (0.1 mole) vinyl butyl ether and 1.05 g (4%) azoisobutyronitrile was sealed into an ampoule and heated to 70-75° for 100 hours. From 5 such ampoules (132 g starting ethers) was recovered 100.8 g of a mixture of monomers while 15.33 g (11.6% of the theoretical) of light-yellow, very viscous product was isolated.

Found %: C 77.98; 78.10; H 9.88; 9.88; N 1.78; 1.79

Found M: 539.5; 530.8

The viscosity of the copolymer was 0.7108 centipoise. The copolymer contains 73.0 mole-% vinyl p-tert-butylphenyl ether and 27.0 mole-% vinyl butyl ether.

SUMMARY

1. The possibility is demonstrated of polymerization and copolymerization of vinyl aryl ethers under the influence of a radical initiator—azoisobutyronitrile.

2. It is shown that in presence of this initiator vinyl aryl ethers can be made to copolymerize with vinyl alkyl ethers.

3. Polymers of vinyl phenyl and vinyl p-tert-butylphenyl ethers, also their copolymers with vinyl ethyl and vinyl butyl ethers, were isolated and characterized. A probable mechanism of their formation is advanced.

4. It is found that vinyl aryl ethers exhibit greater reactivity in copolymerization reactions than vinyl alkyl ethers.

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Received June 20, 1953

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* See C.B. translation page 787.
** See C.B. translation page 1379.
*** See C.B. translation page 697.
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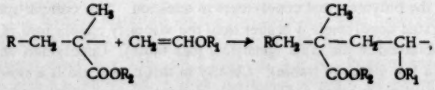
CHEMICAL TRANSFORMATIONS OF UNSATURATED AND HIGH-MOLECULAR COMPOUNDS

COMMUNICATION 3. COPOLYMERIZATION OF METHACRYLIC ACID AND ITS METHYL ESTER WITH VINYL PHENYL ETHER

M. F. Shostakovsky and A. M. Khomutov

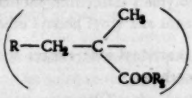
In our previous communications we described the copolymerization of methacrylic acid and its methyl ester with vinyl alkyl ethers [1, 2, 3]. These investigations established that vinyl alkyl ethers enter into copolymerization with methacrylic acid and its derivatives under the influence of benzoyl peroxide notwithstanding that they themselves are not susceptible to polymerization under the influence of oxygen and peroxides. On these observations was based the hypothesis that the initiator of the formation of copolymers of unsaturated components is not a product of breakdown of benzoyl peroxide (C_6H_5, C_6H_5COO; $-O-$), but a complex radical formed on interaction of $C_6H_5COO^{\cdot}$ with methacrylic acid or its esters.

This radical also promotes the polymerization and copolymerization of the original monomers and, in particular, of vinyl alkyl ethers. As we know [4], vinyl ethers do not become activated under the influence of oxygen, peroxides and hydroperoxides in polymerization processes. Notwithstanding that this fact has been adduced in the literature [5] to deny the possibility of free-radical transformations of vinyl ethers, we hold directly opposed views. We think that it is necessary to take account of the nature and specificity of the atoms, of the semi-dissociated molecules and of the free radicals which initiate the process; also of the fact that atomic and molecular oxygen ($-O-$, $-O-O-$), as well as products of breakdown of peroxides and hydroperoxides of the type of C_6H_5COO- do not cause activation of vinyl ethers since their valence belongs to the oxygen. The possibility of formation of $C_6H_5COO^{\cdot}$ by symmetrical cleavage of benzoyl peroxide has been indicated in the literature [6]. Consequently, the nature of the radical and its free valence is the same in these cases and belongs to the oxygen: $-O-$, $-O-O-$; C_6H_5COO-. Evidently, these radicals have little activity for involving vinyl ethers in polymerization and copolymerization reactions. Moreover, transformations of vinyl ethers can take place under the influence of free radicals when the free valence of the latter belongs to carbon, in which case the formation of a polymer chain may be represented by the following schemes:



where R is a radical obtained from benzoyl peroxide; R_1 – is the corresponding alkyl or aryl; R_2 – is a methyl group or hydrogen.

The great activity of this radical



is accounted for by its chemical structure and, among other reasons, by the presence of conjugated double bonds $-C=C$ and $C=O$ [7]. The activity of methyl methacrylate as a copolymerization component has been illustrated in many examples [8].

Great interest is attached to the study of the above-mentioned properties with reference to new representatives of vinyl ethers, for example vinyl phenyl ether $CH_2=CHOC_6H_5$. In contrast to the vinyl alkyl ethers, vinyl phenyl ether polymerizes with difficulty by an ionic mechanism, due to the influence of the benzene ring and the structure of the molecule which causes the oxygen to lose its electron-donating properties and hinders the catalytic action of, for instance, hydrogen chloride [9]. Furthermore, we must mention that vinyl phenyl ether is susceptible

to thermal polymerization [10]. All these points of difference between vinyl phenyl ether and vinyl alkyl ethers justify a special study of the former in copolymerization reactions with methacrylic acid and its methyl ester.

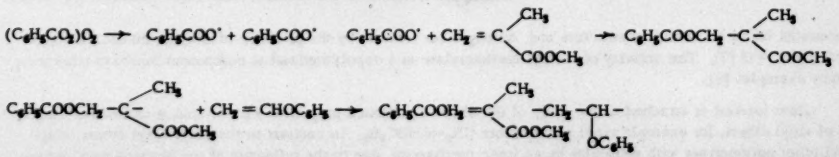
A study of the conditions of polymerization of methyl methacrylate and vinyl phenyl ether in various molar ratios showed that with increasing concentration of vinyl phenyl ether the reaction in some cases proceeds differently than with vinyl alkyl ethers. In all cases substances were obtained which corresponded in elementary composition to products of copolymerization of the original components. Change in the concentration of vinyl phenyl ether led to an increase of the number of vinyl phenyl ether links in the chain of the molecule (see table). It was furthermore established that with molar ratios of 3:1 and 1:1 of methyl methacrylate to vinyl phenyl ether, copolymers were obtained whose degree of polymerization did not exceed that of polymethyl methacrylate. At a 1:3 ratio, i.e., with an excess of vinyl phenyl ether, the polymerization reaction is hindered and low-molecular polymers are formed.

Content of original monomers in mole-%		Yield in %	C in %	H in %	Molar composition of links of molecules		Viscosity	
$CH_2=C(CH_3)COOCH_3$	$CH_2=CHOC_6H_5$				$-CH_2-C(CH_3)(COOCH_3)-$	$-CH_2-CH(OC_6H_5)-$	η_{abs} st/sec	$\eta_{rel.}$
100	–	97.5	60.03 60.05	8.30 8.28	100	–	0.011	1.5011
75	25	76.0	62.70 62.70	7.95 8.16	88.49	11.51	0.021	2.8932
50	50	51.7*	64.42 64.34	7.85 7.98	81.05	19.95	0.015	2.0432
25	75	10.56	67.85 67.70	7.65 7.39	65.38	34.62	0.0081	1.0930
–	100	–	–	–		None		

* 8.21 g vinyl phenyl ether was separated and the amount of methyl methacrylate was found to be 1.07 g.

The evaluation of the degree of polymerization or copolymerization of the investigated products was based on comparison of the viscosity of the solutions of the polymers and copolymers in question. This comparison shows that the viscosities of the solutions of the investigated copolymers is higher than the viscosity of solutions of the corresponding polymers of methyl methacrylate obtained in the same conditions (see table). Copolymers obtained with excess of vinyl phenyl ether, however, have a low viscosity (table). Clearly in this case there is a slowing-down of the formation of chains (table), the yields of copolymers being reduced with increasing concentration of vinyl phenyl ether in the reaction medium. At the same time there is a qualitative change in the copolymer chain due to rise in the number of links of vinyl phenyl ether. Examination of the products of copolymerization shows that separated polymerization is not observed in these conditions and that, in particular, no polymer of methyl methacrylate is formed in these experiments. The resultant copolymers differ from polymers of methyl methacrylate in respect of solubility, for example in a 1:1 mixture of butanol and vinyl phenyl ether, and in fusibility.

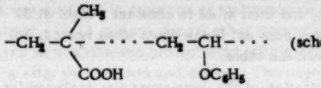
Consequently, the present investigation has shown that vinyl ethers react according to a free-radical mechanism with a radical whose free valences are attached to carbon:

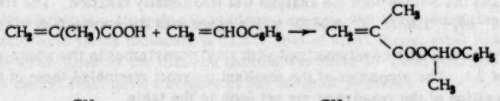


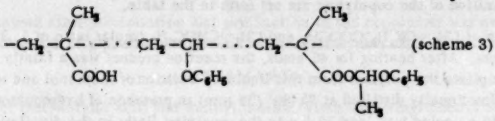
i.e., the nature has been clarified of the radicals which can or cannot involve vinyl ethers in a copolymerization reaction.

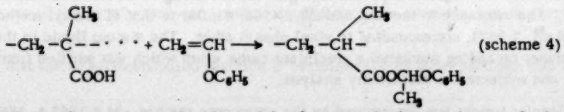
We now go on to consider the data on reaction of methacrylic acid with vinyl phenyl ether. The investigations shows that several concurrent reactions take place in the conditions described below. The reaction mixture contains, apart from copolymers, the original monomers, acylals and phenoxyethylidene methacrylate. The copolymer molecules contains links of: methacrylic acid, vinyl phenyl ether and acylal.

Consequently the copolymerization reaction (scheme 1) is accompanied by formation of acylals (scheme 2); in addition, vinyl alkyl ethers can add on to the carboxyl of polymethacrylic acid (scheme 4):


(scheme 1)


(scheme 2)


(scheme 3)


(scheme 4)

The isolated copolymers have a low molecular weight; for example the copolymers obtained from molar ratios of monomers have a molecular weight of 2265. The yields of copolymers were low.

On the basis of the above observations it follows that reaction of methacrylic acid with vinyl phenyl ether is accompanied by the same types of reactions as in the case of reaction of methacrylic acid with vinyl alkyl ethers [1].

EXPERIMENTAL

The starting materials for the investigations were freshly distilled: methyl methacrylate with b.p. 99.5 - 100°, n_D^{20} 1.4150; d_4^{20} 0.936; methacrylic acid with b.p. 160°; n_D^{20} 1.4313; d_4^{20} 1.0159; acid value 650 mg KOH; vinyl phenyl ether, b.p. 155°, n_D^{20} 1.5225; d_4^{20} 0.9765. Benzoyl peroxide was purified by two reprecipitations; acetone with b.p. 56.5°; n_D^{20} 1.3595 methanol with b.p. 64-65°; n_D^{20} 1.3300; benzene with b.p. 80 - 80.5°; n_D^{20} 1.5010.

Experimental Procedure

Copolymerization was carried out in glass ampoules which were heated in a thermostat at a temperature of 60 ± 1°. The starting substances were brought into reaction in various molar ratios in presence of 0.2% benzoyl peroxide reckoned on the total weight of monomers. The process proceeded continuously until solid or highly viscous products had been formed. At the conclusion of the reaction the ampoules were cooled at 0°. In the same conditions control experiments were run with benzoyl peroxide and, separately, methacrylic acid, methyl methacrylate, and vinyl phenyl ether. The solid reaction products were purified by numerous dissolutions and precipitations until a negative reaction was obtained for the double bond. The polymers and copolymers were then dried to constant weight. The copolymers were not subjected to selective reprecipitation since a polymer of methyl methacrylate was not found. The copolymers were analyzed for C and H. On the basis of the data obtained, calculations were made of the compositon of the copolymers. In addition, the fusibility and viscosity were determined [11]. Solutions obtained after precipitation of the copolymers were analyzed for their content of methyl methacrylate; fractional distillation was applied for separation of the vinyl phenyl ether; part of the solution was evaporated (under vacuum) to establish the possible presence of polymers soluble in a mixture of precipitant and solvent.

Below are presented some data of investigations of the polymerization and copolymerization of various molar ratios of methyl methacrylate to vinyl phenyl ether. In addition, methyl methacrylate and vinyl phenyl ether were separately treated in the same conditions as their mixtures. Methyl methacrylate polymerized. Vinyl

phenyl ether did not polymerize and the original ether was collected after fractionation.

Copolymerization of $CH_2=C(CH_3)COOCH_3$ and $CH_2=CHOC_6H_5$ (1:1 molar ratio). 11.4 g methyl methacrylate and 13.6 g vinyl phenyl ether were taken for copolymerization. The mixture of starting monomers was heated for 40 hours. The reaction products had a viscous consistency. The conditions of copolymerization and the method of purification are set forth above. The copolymer is soluble in a mixture of butanol and vinyl phenyl ether (1:1); the pure polymer of methyl methacrylate does not dissolve in this mixture. The copolymer was completely freed from monomers (test with bromine water), and then dried to constant weight at 30 - 35° (4 mm). The copolymers were analyzed for C and H. The copolymer does not break down when heated, but melts. Yields, composition and viscosities of the copolymers are set forth in the table.

The solution obtained after precipitation of the copolymer was analyzed for its content of methyl methacrylate (by hydrolysis), and the residue from the analysis was fractionally distilled. The fractionation gave a substance with b.p. of 154.5° n_D^{20} – 1.5220 d_4^{20} 0.9672, which agree with the constants of vinyl phenyl ether.

Methyl methacrylate was also copolymerized with vinyl phenyl ether in the above-described conditions but with a molar ratio of 3:1. The properties of the resultant polymer resembled those of the polymer described above. Yield and composition of the copolymer are set forth in the table.

Copolymerization of $CH_2=C(CH_3)COOCH_3$ and $CH_2=CHOC_6H_5$ (molar ratio of 1:3) was performed in the above-described conditions. After heating for 40 hours, the reaction product was a faintly colored liquid. A preliminary attempt to precipitate the polymer from this liquid by addition of methanol and water was unsuccessful; the liquid was therefore fractionally distilled at 75-80° (35 mm) in presence of hydroquinone. In this way 0.95 g substance was collected in a cooled trap, and 12.5 g in the receiving flask; in the distillation flask remained 10.85 g viscous liquid. The substance in the trap had n_D^{20} 1.4165, similar to that of methyl methacrylate; the fraction in the receiver had n_D^{20} 1.5220, corresponding to vinyl phenyl ether. The viscous liquid in the distillation flask was dissolved in acetone; on adding methanol a precipiate came down which was purified from polymers, dried to constant weight and subjected to elementary analysis.

The molecular weight was determined by the cryoscopic method: M = 1563.4 1662.5. The values of molecular weight and the relative viscosity enabled calculation of the magnitude of the constant K_m, which was found to be $0.62 \cdot 10^{-4}$.

We now go on to describe the experimental results of copolymerization of methacrylic acid with vinyl phenyl ether.

Copolymerization of $CH_2=C(CH_3)COOH$ and $CH_2=CHOC_6H_5$ (molar ratio of 3:1). Amounts of reactants taken were 17.1 g methacrylic acid and 7.9 g vinyl phenyl ether in presence of 0.05 g benzoyl peroxide. The reaction conditions were those described above. After heating for 60 hours, the contents of the ampoule had not changed in outward appearance, i.e., they were still liquid. Samples of the liquid were mixed with methanol, benzene, gasoline and diethyl ether but formation of a precipitate or development of turbidity were not observed. The liquid was distilled in vacuum in presence of hydroquinone. At 75-80° (35 mm) 17 g liquid came over which consisted of 12.5 g methacrylic acid and 4.5 g vinyl phenyl ether. In the distillation flask remained a viscous liquid (7.8 g). The latter was dissolved in a mixture of 95% acetone and 5% methanol. Precipitation of the polymer was effected with gasoline (70-80° boiling range). The polymer was then worked up according to the usual procedure. Yield of copolymer 2.5 g. Its elementary analysis gave: %C 66.19; 66.00. H 7.33; 7.32; which corresponds to a molecule containing 57.88% methacrylic acid links and 42.12% vinyl phenyl ether links. The percentage content in the molecules was 62.2 and 37.8 respectively. The copolymer was analyzed for carboxyl groups by the titration method. The methacrylic acid content of the copolymer was found to be 57.19%, in good agreement with the value calculated from the elementary analysis. The acetaldehyde in the copolymer was determined and the value converted to vinyl phenyl ether; the amount of the latter so found was 5.13%.

The solution obtained after precipitation of the copolymer was evaporated in vacuum; evaporation of the solvent left 1.35 g liquid which after fractional distillation had n_D^{20} 1.5028; it was phenoxyethylidene methacrylate [12].

Copolymerization of $CH_2=C(CH_3)COOH$ and $CH_2=CHOC_6H_5$ (molar ratio of 1:1). 10.38 g methacrylic acid, 14.56 g vinyl phenyl ether and 0.05 g benzoyl peroxide were mixed together. The reaction conditions were as described above. The reaction mixture contained a polymer (test by precipitation with gasoline) which was precipitated with gasoline and washed with methanol. The polymer was dried to constant weight. Its

elementary analysis gave (in %): C 69.49; 69.40; H 6.94; 6.93, which corresponds to a copolymer containing 42 wt.-% methacrylic acid and 58 wt.-% vinyl phenyl ether. The copolymer was analyzed for its acetaldehyde content but none was detected. It follows that acylal groupings are absent from the chain of the molecule. The molecular weight of the copolymer as determined by the cryoscopic method was 2265.

Copolymerization of $CH_2=C(CH_3)COOH$ and $CH_2=CHOC_6H_5$ (molar ratio of 1:3). 4.75 g methacrylic acid, 20.25 g vinyl phenyl ether and 0.05 g benzoyl peroxide were heated together for 60 hours. At the conclusion of the heating the mass was distilled in presence of hydroquinone (test for polymer with methanol and gasoline did not give a precipitate). 12.15 g vinyl phenyl ether was collected at 75° (30 mm). The residue in the distillation flask was dissolved in acetone and precipitated with gasoline (distilled at 70-80°). A polymer was separated and weighed 3.5 g after purification and drying. The copolymer had the elementary composition (in %): C 67.04; 67.07; H 6.81; 6.83.

On the basis of the elementary analysis calculations were made of the composition of the copolymer: the content of methacrylic acid links in the molecule is 53.5%, that of vinyl phenyl ether links 46.5%. The content of methacrylic acid links determined by the titration method was 52.03%. Determination of the acetaldehyde and its recalculation to vinyl phenyl ether gave a content of the latter of 10.26%.

The solution obtained after precipitation and purification of the copolymer was evaporated and distilled; from the solution was isolated 2.76 g phenoxyethylidene methacrylate with n_D^{20} 1.5034.

SUMMARY

1. Copolymers of methacrylic acid and methyl methacrylate with vinyl phenyl ether have been prepared.

2. The composition of the copolymers was found to depend upon the concentration of vinyl phenyl ether in the reaction mixture.

3. It was shown that the copolymerization reaction is accompanied by side reactions with formation of acylals.

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Received September 4, 1953

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1-5) See C.B. Translation, pp.: 1) 931; 2) 263; 3) 414; 4) 51; 5) 453.

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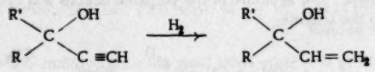
DERIVATIVES OF TERTIARY UNSATURATED ALCOHOLS

COMMUNICATION 2. SYNTHESIS OF METHYL-, ETHYL-, ISOPROPYL-, AND BUTYLDIMETHYLVINYLACETALS

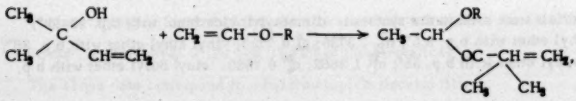
M. F. Shostakovsky and I. A. Shikhiev

A. E. Favorsky and his school [1] have established the conditions for synthesis of substituted allyl alcohols according to the scheme:



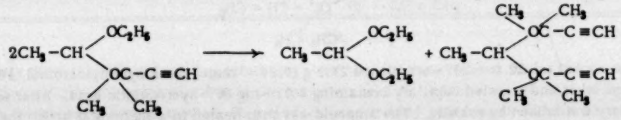
These compounds are valuable starting materials in synthetic organic chemistry [2].

The authors of the present paper aimed at synthesizing substituted allyl acetals on the basis of substituted allyl alcohols and vinyl alkyl ethers according to the scheme:

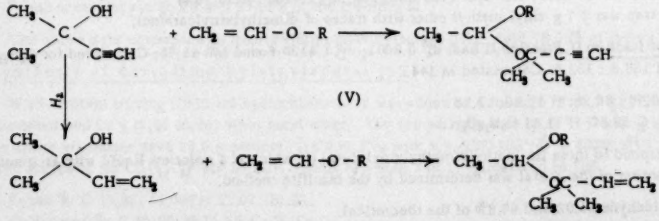


where R = CH_3; C_2H_5; C_3H_7 (iso) and C_4H_9.
Acetals of this series are of great interest and have scarcely been studied.

In our previous communication [3] it was shown that reaction of dimethylethynylcarbinol with vinyl ethyl ether leads to disproportionation of the unsymmetrical acetylenic acetal according to the following scheme:



In the present investigation we compare the properties of the acetylenic and the corresponding substituted allyl acetals. The synthesis of these (V) and other (VI) acetals is based on reaction of dimethylethynylcarbinol and of dimethylvinylcarbinol with vinyl alkyl ethers according to the scheme:

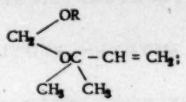


(V)

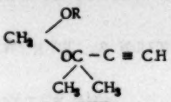
(VI)

These acetals were prepared in presence of a catalyst in the conditions described in the previous communication [3]. This interesting transition from acetylenic acetals to the corresponding substituted allyl acetals and the investigation of their properties enables us to study the reactivity and stability of these compounds.

One of us [4] has carried out similar investigations of acetylenic and the corresponding substituted allyl formals, when it was established that the substituted allyl formals (VII) are more stable than the acetylenic formals (VIII):



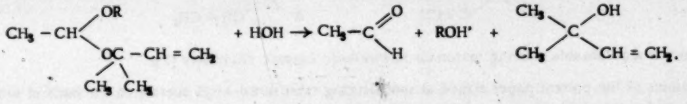
(VII)



(VIII)

Finally, it was of interest to verify and amplify the general concepts about the properties of acetylenic substituted allyl acetals and the corresponding formals.

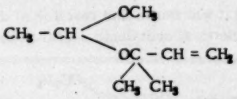
To sum up, therefore, the present investigation has shown that substituted allyl acetals are more stable than the corresponding acetylenic acetals. The structure of the prepared acetals was confirmed by their cleavage to the original components according to the scheme:



EXPERIMENTAL*

The following starting materials were used in the synthesis: dimethylvinylcarbinol with b.p. 98-99°; n_D^{20} 1.4140; d_4^{20} 0.8246; vinyl methyl ether with b.p. 5.5°; n_D^{0} 1.3730; d_4^{0} 0.7725; vinyl ethyl ether with b.p. 36°; n_D^{20} 1.3779; d_4^{20} 0.7531; vinyl isopropyl ether with b.p. 55°; n_D^{20} 1.3862; d_4^{20} 0.7520; vinyl butyl ether with b.p. 93-94°; n_D^{20} 1.4026; d_4^{20} 0.7792.

1. Synthesis of methyldimethylvinylacetal (I)



In an ampoule cooled to −12 to −14° were placed 21.5 g (0.25 mole) dimethylvinylcarbinol, 16 g (0.277 mole vinyl methyl ether and a sealed capillary containing 0.016 mg 30% hydrochloric acid. After sealing the ampoule, the capillary was broken by shaking. The ampoule was then heated in a thermostat at 65° for 9.5 hours. The next day the ampoule was cooled to −10° and opened; the contents were neutralized with calcined potassium carbonate and distilled. The volatile fraction was collected in a trap cooled to −10 to −14°; the following were collected:

Fr. I., b.p. to 27° (9-10 mm); 3.2 g; n_D^{20} 1.4122

Fr. II., b.p. 28-29° (9-10 mm); 132-133° (760 mm); 28g; n_D^{20} 1.4130 (yield 78%)

The material in the trap was 2.7 g vinyl methyl ether with traces of dimethylvinylcarbinol.

Examination of fraction II. Fraction II had: d_4^{20} 0.8601; n_D^{20} 1.4130; Found MR 41.75; Calculated for $C_8H_{16}O_2$ MR 41.963; Found M 138.8; 132.5; Calculated M 144.

Found %: C 66.73; 66.98; H 11.09; 11.18

Calculated %: C 66.66; H 11.11 $C_8H_{16}O_2$.

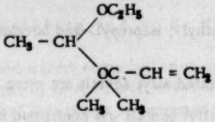
The data correspond to those for methyldimethylvinylacetal (I) which is a colorless liquid with an ethereal odor. The acetaldehyde content of the acetal was determined by the bisulfite method.

Found: acetaldehyde 94.02 and 93.8% of the theoretical.

Vinyl methyl ether was synthesized by P. V. Tyupaev to whom we convey our thanks.

* Senior Assistant Z. S. Volkova participated in the work.

2. Synthesis of ethyldimethylvinylacetal (II)



To a mixture of 43 g (0.5 mole) dimethylvinylcarbinol and 36 g (0.5 mole) vinyl ethyl ether at room temperature and with constant stirring was added 0.012 ml 30% hydrochloric acid (during this operation the temperature rose to 52°), after which the mixture was left overnight. The next day the reaction mixture was dried with potassium carbonate and the filtered product (79.0 g) was distilled. The volatile products were collected in a trap cooled to −15 to −16°.

Fr. I., b.p. 21-26° (11-12 mm); 2.2 g; n_D^{20} 1.4152.
Fr. II., b.p. 40-41° (11-12 mm); 146-147° (760 mm); 65 g ; n_D^{20} 1.4119 (yield 82.82%)
Residue − 1.4 g.

The material in the trap was mainly unreacted vinyl ethyl ether (8.0 g) with traces of dimethylvinylcarbinol.

Examination of fraction II The fraction with b.p. 40-41° had: d_4^{20} 0.8502; n_D^{20} 1.4119; Found MR 46.22; Calculated for $C_9H_{18}O_2F$ MR 46.581; Found M 149.0 ; 147.3; Calculated M 158.

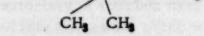
Found %: C 68.32, 68.30, H 11.97, 11.89.
Calculated %: C 68.35 , H 11.39 $C_9H_{18}O_2$.

The acetaldehyde content of the acetal was also determined by the bisulfite method.

Found : acetaldehyde 97.98 and 97.43% of the theoretical.

The above data correspond to ethyldimethylvinylacetal (II).

3. Synthesis of isopropyldimethylvinylacetal (III)



Exactly the same ratios of starting substances were used for this synthesis as for the preceding synthesis (II). After addition of 0.012 ml hydrochloric acid the temperature of the mixture rose to 62°. After working up and distillation by the above-described method, 68 g product was obtained with b.p. 45-46° (10-11 mm) and 156-157° (760 mm)with the following constants: d_4^{20} 0.8422; n_D^{20} 1.4126; Found MR 50.88; calculated for $C_{10}H_{20}O_2F$ MR 51.199; Found M 163.50; 164.7 ; Calculated M 172.0.

Found %: C 69.96 69.76; H 11.30; 11.48.
Calculated %: C 69.76; H 11.62. $C_{10}H_{20}O_2$.
Found acetaldehyde 95.26 and 97.98% of the theoretical.

The above data correspond to isopropyldimethylvinylacetal (III); yield 79.06% of theory.

4. Synthesis of butyldimethylvinylacetal (IV)

With constant stirring 0.012 ml hydrochloric acid was added to a mixture of 21.5 g (0.25 mole) dimethylvinylcarbinol and 25 g (0.25 mole) vinyl butyl ether. The temperature rose to 70°. Working up and distillation by the above procedure gave 38.5 g product (yield 80.8%) with b.p. 182-183°; d_4^{20} 0.8396; n_D^{20} 1.4148; Found MR 55.46; Calculated for $C_{11}H_{22}O_2F$ MR 55.817; Found M 180.0; 179.1; Calculated M 186.

Found %: C 70.98; 71.00; H 11.01 10.97.
Calculated %: C 70.96; H 11.18 $C_{11}H_{22}O_2$.
Found acetaldehyde 99.80 and 96.93% of the theoretical.

The constants found correspond to butyldimethylvinylacetal . It should be mentioned that all of the four substituted allyl acetals are stable, possess a characteristic ethereal odor and decolorize a weak solution of $KMnO_4$ and bromine water. The properties of the prepared acetals are being studied.

SUMMARY

1. For the first time the methyl-, ethyl-, isopropyl- and butyldimethylvinylacetals have been prepared and characterized.

2. It was established that the substituted allyl acetals are more stable than the acetylenic acetals.

3. The structure of the substituted allyl acetals was confirmed by their hydrolytic cleavage into the original components.

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Received July 29, 1953

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* See C.B. translation, page 61.

** " " " " 943.

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DESTRUCTIVE HYDROGENATION OF TOLUENE UNDER HIGH HYDROGEN PRESSURE

M. G. Gonikberg and V. E. Nikitenkov

In 1929 Hoffman and Lang [1] published a short communication on their experiments on destructive hydrogenation of toluene in the absence of catalysts in an autoclave at 470-485° and a hydrogen pressure of up to 200-250 atm. Under these conditions up to 50% of the toluene is converted into benzene; the gaseous reaction product contained, apart from hydrogen, methane and ethane, Also present among the reaction products (in very small amounts) were diphenyl, monomethyldiphenyl and ditolyl. Hydrogenation of toluene to methylcyclohexane was not observed. In experiments carried out in the absence of hydrogen at 470°, the authors observed the formation in small quantity of hydrogen and ditolyl.

In 1938 Nemtsov [2] published the results of an investigation of the homogeneous destructive hydrogenation of toluene under hydrogen pressure at temperatures close to 500° (the pressure range was not indicated). According to Nemtsov's data the reaction velocity does not depend upon the presence of a metallic packing and to a first approximation may be expressed by an equation for bimolecular reaction between toluene and hydrogen. The constant K_2 of the bimolecular reaction satisfies the equation:

$$\log K_2 = 15.54 - \frac{66000}{4.57\,T},$$

where K_2 is expressed in liters·mole^{-1}·min^{-1}.

Calculation of the exponential factor by the theory of collisions led the author to the conclusion that each active collision brings about transformation of 60 molecules of hydrocarbon. Nemstov did not consider, however, that a chain mechanism involving the intermediate formation of atoms or free radicals was likely to account for this fact.

In the present research the homogeneous destructive hydrogenation of toluene was studied at 455-490° and at hydrogen pressures up to 1350 atm. On the basis of the results obtained, a chain mechanism is advanced for this process.

EXPERIMENTAL

Apparatus and experimental procedure

The investigation was carried out in an autoclave of stainless steel with a capacity of about 160 ml and fitted with a hydraulic seal. The toluene was charged into the reactor which was then sealed; the pressure of the hydrogen was thereupon raised with the help of a pressure apparatus fed from a gasholder. The toluene was previously distilled in a rectifying column with an efficiency of 30 theoretical plates and was characterized by the following constants: b.p. 110.4–110.6° (760 mm); n_D^{20} 1.4963. According to the literature [3]: it has b.p. 110.626° (760 mm); n_D^{20} 1.49693. The initial hydrogen pressures in the different experiments varied between 100 and 600 atm. The reactor was then placed in an electric furnace and heated to the required temperature which was measured with a thermocouple in a long sheath inside the reactor and passing through the hydraulic seal. The temperature was kept constant to ± 2°. The reactor was held at the experimental temperature for a specified period and then cooled with water. The working pressure ranged from 280 to 1350 atm. At the conclusion of the experiment the pressure was slowly dropped to atmospheric; the liquid products were fractionated in a rectifying column with an efficiency of 30 theoretical plates. When the initial hydrogen pressures were 100 and 250 atm. (working pressure 280 and 650 atm.), the liquid reaction products contained benzene and toluene together with about 1% of high-boiling components; in the majority of experiments carried out with an initial hydrogen pressure of 450 and 600 atm. (working pressure 1100 and 1350 atm), methylcyclohexane was found in the reaction products in addition. Chromatographic separation of the aromatic hydrocarbons from the methylcyclohexane fraction followed by refractionation of the latter gave pure methylcyclohexane (b.p. 100.7-100.9° (760 mm); n_D^{20} 1.4229; d_4^{20} 0.7690; the literature [3] reports: b.p. 100.937° (760 mm); n_D^{20} 1.42305; d_4^{20} 0.76936.

Results of the investigation

a) Influence of duration of experiment and the pressure upon the reaction velocity. Results of experiments at 455° using a constant amount of toluene (30 g) charged into the reactor are set forth in Table 1. The yield of benzene at constant hydrogen pressure increases substantially linearly with the duration of the experiment (Fig. 1). In the last column of Table 1 are set forth the ratios of reaction velocity to hydrogen concentration (in hour^{-1}). Within the limits of error this ratio remains constant for each experimental series (at constant pressure), but de-

creases with rising pressure (concentration) of hydrogen. Thus the reaction velocity increases with rising hydrogen concentration, although not proportionally to the latter but slightly more slowly. For example, with a 3,8-fold increase of hydrogen concentration the reaction velocity rises approximately 2,5 times.

It follows from the data of Table 1 that homogeneous destructive hydrogenation of toluene is not a bimolecular reaction, for which the velocity would necessarily have been proportional to the concentration of toluene and hydrogen.

TABLE 1

Destructive hydrogenation of toluene at 455 ° and various hydrogen pressures

P_{H_2} atm. (working)	Duration, in hours	Yield of benzene		Amount of hydrogen in moles			moles C_6H_6 / moles $H_2 \cdot \tau$ (mean) hour^{-1}
		in mol-%	in mole	initial	final*	mean	
280	3	10,7	0,0349	0,557	0,522	0,539	0,0215
280	5	12,6	0,0409	0,557	0,516	0,536	0,0153
290	7	23,3	0,0761	0,585	0,509	0,547	0,0199
290	8	26,0	0,0845	0,585	0,500	0,542	0,0195
280	11,6	34,9	0,114	0,557	0,443	0,500	0,0196
650	3**	19,8	0,0645	1,290	1,226	1,258	0,0171
"	5	32,6	0,106	1,290	1,184	1,237	0,0171
"	7	43,5	0,142	1,290	1,148	1,219	0,0166
"	10,5	65,1	0,212	1,290	1,078	1,184	0,0170
1100	3	23,2	0,0755	2,110	2,035	2,073	0,0122
"	3	24,1	0,0787	2,110	2,031	2,070	0,0127
"	3	19,2	0,0625	2,110	2,048	2,079	0,0101
"	5	38,5	0,126	2,110	1,984	2,047	0,0123
"	5,5	43,6	0,142	2,110	1,968	2,039	0,0126
1350	3,5	33,4	0,109	2,690	2,581	2,635	0,0118
"	3,5	32,5	0,106	2,690	2,584	2,637	0,0114
"	5,5	58,4	0,191	2,690	2,409	2,595	0,0134

* Calculated on the yield of benzene.

** Mean of 4 experiments.

b) Influence of initial toluene concentration upon the reaction velocity. The dependence of the reaction velocity on the toluene concentration was examined by carrying out experiments at 455° with various initial charges of toluene (20,30 and 40 g). The hydrogen concentration during this series did not vary by more than 10 % from the mean value. Results of these experiments are set forth in Table 2.

It follows from Table 2 that the reaction velocity increases with increasing toluene concentration; the values in the last column, however, indicate the absence of direct proportionality between the concentration of (charged in) toluene and the reaction velocity. A twofold increase of the charge of toluene in one experimental series speeded up the reaction 1.58 times; in a second series the speed increased 1,44 times; the average speed-up was 1,5 times; consequently the reaction velocity is approximately proportional to the square root of the toluene concentration. This effect could not be deduced from inspection of the data of Table 1 due to the relatively small changes of mean concentrations of toluene during the majority of the experiments in each series.

TABLE 2

Destructive hydrogenation of toluene at 455° and various initial concentrations of toluene

P_{H_2} in atm., (working)	Duration in hours,	Charge of toluene, in g	Yield of benzene		Amount of hydrogen, in moles			moles C_6H_6 / moles $H_2 \cdot \tau$ hr^{-1}
			in mole-%	in mole	initial	final	mean	
270	8.5	20	31.2	0.0678	0.612	0.544	0.578	0.0138
290	8	30	26.0	0.0845	0.585	0.500	0.542	0.0195
290	8.5	40	26.6	0.0851	0.500	0.415	0.458	0.0219
640	5	20	43.5	0.0945	1.420	1.336	1.373	0.0138
650	5	30	32.6	0.106	1.290	1.184	1.237	0.0171
650	5	40	25.2	0.110	1.162	1.052	1.108	0.0198

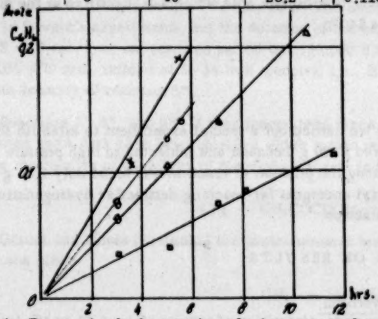


Fig. 1. Destructive hydrogenation of toluene at 455° under pressure: □ – 280 atm; Δ – 650 atm; ○ – 1100 atm; X – 1350 atm.

c. Investigation of the influence of the surface/volume ratio (S/V) on the reaction velocity. It was considered desirable to confirm the existing data for the homogeneity of the process under investigation. For this purpose experiments were carried out with addition of turnings from the same batch of stainless steel. The area of the surface of the turnings, evaluated from the measurement of the parameters of 100 cuttings, was about 18 cm^2/g. The area of the internal surface of the reactor was about 260 cm^2.

Below are set forth the results of an examination at 464° with an initial hydrogen pressure of 250 atm. and a reaction period of 4.25 hours:

S cm^2	260	400	900
S/V cm^{-1}	1.6	2.5	5.6
Yield C_6H_6, expressed as mol.-% to C_7H_8 charged	46.8	44.8	52.6

The conclusion to be drawn from these results is that the size of the surface and its ratio to the volume has no marked influence upon the reaction velocity. The slight increase in benzene yield at S/V = 5.6 is scarcely outside the limits of experimental error.

TABLE 3

Destructive hydrogenation of toluene at 490° (working pressure of 670 atm.)

τ duration in hours	Yield of benzene		Amount of hydrogen, in mole			moles C_6H_6 / moles $H_2 \cdot \tau$ (mean) $hour^{-1}$
	in mol. %	in mole	initial	final	mean	
1	36.1	0.118	1.290	1.172	1.231	0.0958
1.5	50.1	0.163	1.290	1.127	1.209	0.0902
2	61.2	0.200	1.290	1.090	1.190	0.0840

d) Influence of temperature on the reaction velocity. Results of experiments carried out at 490° with a toluene charge of 30 g are set forth in Table 3.

Comparison of the data of Tables 1 and 3 shows that rise of temperature from 455 to 490° leads to a very considerable increase of reaction velocity. The energy of activation was not determined in this investigation.

e) Investigation of the high-boiling reaction products. It appeared of interest to investigate the high-boiling reaction products whose structure ought to give an indication of the radicals formed in the course of destructive

hydrogenation of toluene. Examination of the high-boiling residues after rectification of the reaction products established the presence of diphenyl and ditolyl.

The isolated diphenyl was characterized by its m.p. of 68.5-70° (the literature gives 70.0°). A mixed test with pure diphenyl did not give a depression of m.p.

Results of analysis.
Found %: C 93.29; H 6.73
Calculated %: C 93.46; H 6.54 $C_{12}H_{10}$.

Ditolyl was separated by fractionation of the high-boiling residue (fraction 277-280° at 760 mm); n_D^{20} 1.6003; d_4^{20} 1.0125.

Results of analysis.
Found %: C 92.35; 92.41; H 7.64; 7.52.
Calculated %: C 92.26; H 7.74. $C_{14}H_{14}$.

Oxidation of the ditolyl with chromic acid mixture gave terephthalic acid which was identified as the dimethyl ester — m.p. of ester 138-139.5° (the literature gives 140°).

Results of analysis:
Found %: C 61.65; H 5.25
Calculated %: C 61.85; H 5.19. $C_{10}H_{10}O_4$.

Dibenzyl was not found among the reaction products. We carried out a special experiment to establish the causes of the absence of dibenzyl. 5 g dibenzyl was dissolved in 30 g benzene and subjected to high pressure (working pressure of 580-560 atm.) at 460° for 5 hours. Among the products of reaction was found only 1.34 g dibenzyl. In our experimental conditions, therefore, dibenzyl undergoes far-reaching destructive hydrogenation, and this may account for its absence from the products of reaction.

EVALUATION OF RESULTS

a) Thermal decomposition of toluene in absence of hydrogen.

In 1948 Szwarc [4] studied the induction period of thermal decomposition of toluene (from 0.01 to 1% decomposition) in vacuum at temperatures of 738-864° by passing toluene vapor through a heated quartz tube and cooling the reaction products. The gaseous reaction products comprised 59-62% hydrogen and 38-41% methane. The liquid reaction products contained benzene and dibenzyl (1 mole of dibenzyl to 1 mole of gas formed). The author arrived at the conclusion that the reaction involves the following steps:

$$C_6H_5CH_3 \xrightarrow{1} C_6H_5CH_2^{\cdot} + H^{\cdot}$$

$$C_6H_5CH_3 + H^{\cdot} \xrightarrow{2} C_6H_5CH_2^{\cdot} + H_2$$

$$C_6H_5CH_3 + H^{\cdot} \xrightarrow{3'} C_6H_6 + CH_3^{\cdot}$$

or

$$C_6H_5CH_3 + H^{\cdot} \xrightarrow{3''} C_6H_5^{\cdot} + CH_4$$

$$CH_3^{\cdot} + C_6H_5CH_3 \xrightarrow{4'} CH_4 + C_6H_5CH_2^{\cdot}$$

or

$$C_6H_5^{\cdot} + C_6H_5CH_3 \xrightarrow{4''} C_6H_6 + C_6H_5CH_2^{\cdot}$$

$$2C_6H_5CH_2^{\cdot} \xrightarrow{5} C_6H_5CH_2CH_2C_6H_5$$

The suggestion that rupture of the C – C bond

$$C_6H_5CH_3 \longrightarrow C_6H_5^{\cdot} + CH_3^{\cdot}$$

was the first step in the reaction was refuted by data for the composition of the gaseous reaction products (60% hydrogen), whereas the author's proposed scheme satisfactorily accounted for the formation of the above-mentioned compounds and for the amount of dibenzyl formed. Ditolyl was not detected.

As already indicated above, Hoffmann and Lang [1], who thermally decomposed toluene in an autoclave at 470° found ditolyl among the reaction products, but not dibenzyl. In the present research we, too, found ditolyl among

the products of thermal decomposition of toluene at 480°. The absence of dibenzyl may have been due to its thermal instability.

Of great interest is the formation of ditolyl during thermal decomposition of toluene. Detachment of hydrogen from the benzene ring by reaction under our experimental conditions

$$C_6H_5CH_3 \xrightarrow{1'} H^{\cdot} + C_6H_4CH_3^{\cdot}$$

is extremely improbable, although we cannot altogether exclude its possibility. It seemed to us, however, that formation of ditolyl may also be explained by supplementing Szwarc's scheme by the following reactions:

$$C_6H_5CH_3 + H^{\cdot} \xrightarrow{3'''} H_2 + C_6H_4CH_3^{\cdot}$$

$$C_6H_4CH_3^{\cdot} + C_6H_5CH_3 \xrightarrow{4'''} C_6H_5CH_3 + C_6H_5CH_2^{\cdot}$$

$$2C_6H_4CH_3^{\cdot} \xrightarrow{6} CH_3C_6H_4C_6H_4CH_3$$

The absence of ditolyl from the products of Szwarc's experiments may be accounted for by the very low velocity of reaction 3''' in vacuum. We carried out the decomposition of toluene at considerably lower temperatures than in Szwarc's experiments, but the duration of the experiments was 7 hours as against Szwarc's contact period of 0.3–0.9 sec, i.e., our reaction period was 100,000 times greater; the toluene pressure in our experiments was 325-370 atm, instead of 3 - 14 mm mercury, i.e., it was also tens of thousands of times higher than could occur for the velocity of reaction 3'''.

Reactions 3', 3'', and 3''', if they indeed take place, constitute an extremely interesting type of radical reactions. In recent years data have been obtained which makes reactions of this type highly probable. In an investigation of the mechanism of photolysis of biacetyl, Blacket and Bell [5] arrived at the following hypothesis for the reaction:

$$CH_3^{\cdot} + CH_3COCOCH_3 \longrightarrow CH_3COCH_3 + CH_3CO^{\cdot}$$

Gomer and Noyes [6] studied the photochemical breakdown of $Hg(CH_3)_2$ and concluded that the following reaction took place

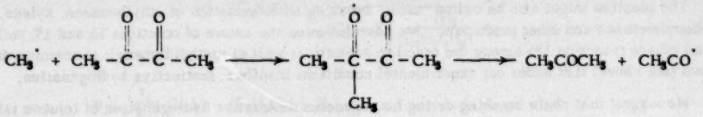
$$CH_3^{\cdot} + Hg(CH_3)_2 \longrightarrow C_2H_6 + Hg + CH_3^{\cdot}$$

or

$$CH_3^{\cdot} + Hg(CH_3)_2 \longrightarrow A\,(\text{unstable complex})$$

$$CH_3^{\cdot} + A \longrightarrow C_2H_6 + Hg + 2CH_3^{\cdot}\ [\text{or } CH_3^{\cdot} + HgCH_3^{\cdot} \text{ or } Hg(CH_3)_2].$$

After analyzing the foregoing data, Darwent [7] suggested that reactions of the type in question involve addition of an atom or radical to the molecule with formation of an unstable free radical which then breaks down, for example



If this hypothesis is accepted, then reactions 3', 3'', and 3''' could have occurred during the decomposition of toluene (depending evidently on the point of attack of the H atom).

Using the concepts discussed above, we are able to formulate a scheme for a chain mechanism of the destructive hydrogenation of toluene which is in satisfactory accord with the data which we obtained for the kinetics of this reaction.

b) Destructive hydrogenation of toluene. If we accept the proposed reaction scheme for thermal decomposition of toluene, then it is clear that in presence of hydrogen under pressure there will be interaction between radicals, formed by thermal decomposition, with molecular hydrogen (also with molecules of toluene and reaction products). Reaction with molecules of H_2 lead to formation of atomic hydrogen and in consequence to the development of a chain reaction.

We suggest the following scheme as probable for the destructive hydrogenation of toluene:

$$C_6H_5CH_3 \xrightarrow{1} C_6H_5CH_2^{\cdot} + H^{\cdot}\ \text{development of a chain}\ *$$

* We could also write: $C_6H_5CH_3 \xrightarrow{1'} C_6H_5CH_3^{\cdot} + H^{\cdot}$ (see above).

$$H^{\cdot} + C_6H_5CH_3 \xrightarrow{2} C_6H_5CH_2^{\cdot} + H_2$$

$$\xrightarrow{3} C_6H_4CH_3^{\cdot} + H_2$$

$$\xrightarrow{4} C_6H_6 + CH_3^{\cdot}$$

$$\xrightarrow{5} C_6H_5^{\cdot} + CH_4$$

$$H_2 + C_6H_5CH_2^{\cdot} \xrightarrow{6} C_6H_5CH_3 + H^{\cdot}$$

$$H_2 + C_6H_4CH_3^{\cdot} \xrightarrow{7} C_6H_5CH_3 + H^{\cdot}$$

$$H_2 + CH_3^{\cdot} \xrightarrow{8} CH_4 + H^{\cdot}$$

$$H_2 + C_6H_5^{\cdot} \xrightarrow{9} C_6H_6 + H^{\cdot}$$

$$C_6H_5CH_3 + C_6H_4CH_3^{\cdot} \xrightarrow{10} C_6H_5CH_2^{\cdot} + C_6H_5CH_3$$

$$C_6H_5CH_3 + CH_3^{\cdot} \xrightarrow{11} C_6H_5CH_2^{\cdot} + CH_4$$

$$C_6H_5CH_3 + C_6H_5^{\cdot} \xrightarrow{12} C_6H_5CH_2^{\cdot} + C_6H_6$$

$$H^{\cdot} + CH_4 \xrightarrow{13} CH_3^{\cdot} + H_2$$

$$H^{\cdot} + C_6H_6 \xrightarrow{14} C_6H_5^{\cdot} + H_2$$

$$2\,C_6H_5^{\cdot} \xrightarrow{15} (C_6H_5)_2$$

$$2C_6H_5CH_2^{\cdot} \xrightarrow{16} (C_6H_5CH_2)_2$$

$$2C_6H_4CH_3^{\cdot} \xrightarrow{17} (C_6H_4CH_3)_2$$

$$2CH_3^{\cdot} \xrightarrow{18} C_2H_6$$

Breaking of the chain

The reaction might also be called "cross" breaking with formation of ethylbenzene, xylene, methyldiphenyl, diphenylmethane and other products*. We have followed the course of reactions 15 and 17; Hoffmann and Lang [1] found ethane (reaction 18) among the reaction products as well as methyldiphenyl; concerning dibenzyl, we have shown (see above) that under our experimental conditions it suffers destructive hydrogenation.

We suggest that chain breaking during homogeneous destructive hydrogenation of toluene takes place preferentially at the tolyl radicals according to reaction 17.

Under steady conditions with considerable length of chain:

$$\frac{d(C_6H_4CH_3)}{d\tau} = K_3(H)(C_6H_5CH_3) - K_7(H_2)(C_6H_4CH_3) - K_{10}(C_6H_5CH_3)\cdot(C_6H_4CH_3) = 0.$$

Hence

$$(C_6H_4CH_3) = \frac{K_3(H)(C_6H_5CH_3)}{(H_2)\left[K_7 + K_{10}\dfrac{(C_6H_5CH_3)}{(H_2)}\right]} \qquad (1)$$

From the balance of chain initiation and breakage

$$K_1(C_6H_5CH_3) = K_{17}(C_6H_4CH_3)^2 \qquad (2)$$

* Here we do not write the reactions opposite to 11 and 12 (due to the low activity of benzyl radicals), nor the heterogeneous hydrogenation of toluene to methylcyclohexane.

we find, taking (1) into account:

$$(H) = \sqrt{\frac{K_1}{K_{17}}} \cdot \frac{K_7 + K_{10}\frac{(C_6H_5CH_3)}{(H_2)}}{K_9} \cdot \frac{(H_2)}{\sqrt{(C_6H_5CH_3)}} \quad (3)$$

We write the expression for the reaction velocity

$$w = (K_4 + K_8)(H)(C_6H_5CH_3) \quad (4)$$

or

$$w = \sqrt{\frac{K_1}{K_{17}}} \cdot \frac{(K_4 + K_8)}{K_9} \cdot (H_2) \cdot \sqrt{(C_6H_5CH_3)} \cdot \left[K_7 + K_{10}\frac{(C_6H_5CH_3)}{(H_2)}\right] \quad (5)$$

From this it appears that the reaction velocity to a first approximation (without allowing for the expression in the square brackets) must be proportional to the hydrogen concentration and to the square root of the toluene concentration. Taking into account the expression in the square brackets in equation (5), we reach the conclusion that the reaction velocity must increase slower than linearly with increasing hydrogen concentration. This has actually been observed to be the case.

It can be shown that equations analogous to (5) for the reaction velocity are also obtained on the assumption that preferential chain breaking occurs not at tolyl but at methyl and phenyl radicals, as well as with "cross" breakages with participation of these radicals. The reaction velocity equation takes on another form in the event of preferential chain breakage at benzyl radicals; we then have:

$$K_1(C_6H_5CH_3) = K_{16}(C_6H_5CH_2)^2 \quad (6)$$

$$(C_6H_5CH_2) = \frac{(C_6H_5CH_3)[K_6(H) + K_{10}(C_6H_4CH_3) + K_{11}(CH_3) + K_{12}(C_6H_5)]}{K_6(H_2)} \quad (7)$$

On the condition that reactions 13 and 14 can be neglected, we find:

$$CH_3 = \frac{K_4(H)}{K_{11} + K_8\frac{(H_2)}{(C_6H_5CH_3)}}; \qquad C_6H_5 = \frac{K_5(H)}{K_{12} + K_9\frac{(H_2)}{(C_6H_5CH_3)}}$$

$$(C_6H_4CH_3) = \frac{K_6(H)}{K_{10} + K_7\frac{(H_2)}{(C_6H_5CH_3)}}$$

Hence

$$w = \sqrt{\frac{K_1}{K_{16}}}(H_2) \cdot (C_6H_5CH_3) \times$$

$$\times \frac{K_6(K_4 + K_8)}{\left[K_9 + \frac{K_8K_{10}}{K_{10} + K_7\frac{(H_2)}{(C_6H_5CH_3)}} + \frac{K_4K_{11}}{K_{11} + K_8\frac{(H_2)}{(C_6H_5CH_3)}} + \frac{K_5K_{12}}{K_{12} + K_9\frac{(H_2)}{(C_6H_5CH_3)}}\right]} \quad (8)$$

Inspection of equation (8) leads to the conclusion that in the event of preferential chain breakage at the benzyl radicals, the reaction velocity must increase at a rate higher than is represented by a linear relation when the hydrogen concentration is increased. This is not confirmed by experiment. Consequently the kinetic considerations and the chemical investigation of the reaction products point to dibenzyl being formed under our experimental conditions only to an insignificant extent and without influencing the kinetics of the reaction.

Equation (5) and similar equations for preferential breakage at the methyl and phenyl radicals derived on the assumption of the insignificant extents of reactions 13 and 14 which constitute the reverse of reactions 8 and 9)

are consistent with the experimental data obtained in the present investigation.

The authors express their thanks to A. E. Gavrilova for advice during the experimental work, and to V. V. Voevodsky for advice and help in working out the scheme for the chain mechanism of the investigated reaction.

Assistance in the work was given by draftsman-designer A. A. Opekunov and fitter V. A. Kuznetsov.

SUMMARY

1. The homogeneous destructive hydrogenation of toluene was investigated at high hydrogen pressures.

2. A chain mechanism is advanced for the investigated process on the basis of which an equation for the reaction velocity is derived which is consistent with the experimental results.

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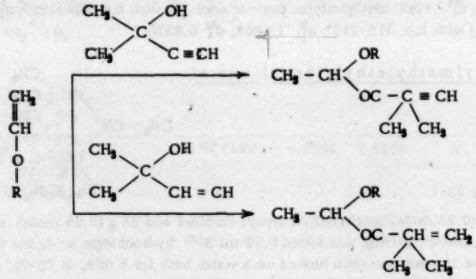
DERIVATIVES OF TERTIARY UNSATURATED ALCOHOLS

COMMUNICATION 3. SYNTHESIS OF DIMETHYLETHYNYL(VINYL)- AND METHYLETHYLETHYNYL(VINYL)-tert-BUTYL ACETALS

M. F. Shostakovsky, I. A. Shikhiev and V. I. Belyaev

The present investigation forms a continuation of our studies in the field of vinyl ethers [1]. With the objective of ascertaining the reactivity of vinyl ethers of tertiary alcohols, we have studied their reaction with tertiary acetylenic and olefinic carbinols.

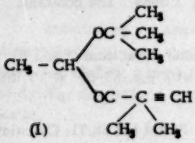
In our previous communications we established that vinyl ethers of primary and secondary alcohols in presence of traces of hydrochloric acid react with acetylenic [2] and olefinic [3] carbinols to form the corresponding acetals according to the scheme:



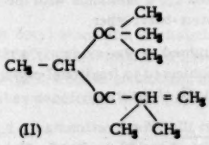
where R = CH_3; C_2H_5; C_3H_7 (iso) C_4H_9-(iso) and C_4H_9-n.

The constants of the prepared acetylenic and olefinic acetals exhibit the following regularities: 1) the boiling points of the olefinic acetals are lower than those of the corresponding acetylenic acetals; 2) the specific gravities and refractive indices of the olefinic acetals are also lower than those of the corresponding acetylenic acetals.

The aim of the present investigation was to synthesize and study the properties of the following acetylenic and olefinic acetals:



(I)



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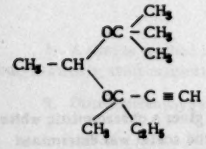

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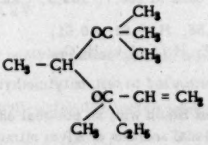
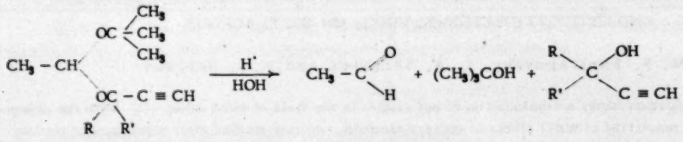


(IV)

The investigation resulted in the preparation and characterization of tert-butyldimethylmethylethylethynyl acetal and tert-butyldimethylmethylethylvinyl acetal. It was established that the prepared acetylenic and olefinic acetals, like those previously investigated [2,3], also exhibit regular differences in specific gravity and refractive index. It may be mentioned that the acetylenic acetals are less stable and turn yellow on standing, whereas the olefinic acetals remain clear after standing for the same period.

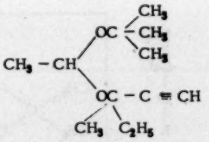
It has thus been shown that acetals containing the vinyl group are more stable. The structure of the prepared acetals was confirmed by their hydrolytic cleavage into the original components according to the equation:



EXPERIMENTAL*

The following starting substances were used for synthesis: vinyl-tert-butyl ether with b.p. 75-75.8°; n_D^{20} 1.3926; d_4^{20} 0.7699; dimethylethynyl carbinol [4] with b.p. 102-103°; n_D^{20} 1.4208; d_4^{20} 0.8580; dimethylvinyl carbinol [4] with b.p. 98-99°; n_D^{20} 1.4140; d_4^{20} 0.8242; methylethylethynylcarbinol [4] with b.p. 120-121°; n_D^{20} 1.4285; d_4^{20} 0.8697; methylethylvinylcarbinol [4] with b.p. 115-116°; n_D^{20} 1.4258; d_4^{20} 0.8375.

Synthesis of tert-butylmethylethylethynyl acetal



To a mixture of 24.5 g (0.25 mole) methylethylethynyl carbinol and 25 g (0.25 mole) vinyl-tert-butyl ether at room temperature and with constant stirring was added 0.02 ml 30% hydrochloric acid; the temperature of the reaction mixture rose to 64°. The mixture was then heated on a water bath for 5 min. at 70-75° before leaving overnight. The next day the reaction mixture was dried with potassium carbonate; 47.5 g of the product was then fractionated in vacuum from a Favorsky flask; the volatile products were trapped in a coil cooled to −7°. The following fractions were collected:

Fr. I., b.p. up to 79° (12-13 mm); 2.5 g; n_D^{20} 1.4268
Fr. II., b.p. up to 80-81° (12-13 mm); 8.5 g; n_D^{20} 1.4270
Fr. III., b.p. up to 82-89° (12-13 mm); 32.0 g; n_D^{20} 1.4286
Residue 2.0 g

In the trap was collected 1.2 g substance with the following constants; d_4^{20} 0.7720; n_D^{20} 1.3984. The constants are close to those of vinyl-tert-butyl ether.

Fraction I was not examined; it was evidently a mixture of unreacted starting compounds. Fractions II and III were combined and twice subjected to fractional crystallization to give mainly a product with b.p. 88-89° at 13 mm in the amount of 30 g or 60.6% of theory.

Examination of fraction III. The fraction had b.p. 88-89°; d_4^{20} 0.8694; n_D^{20} 1.4290; Found MR 58.71; Calculated for $C_{11}H_{22}O_2F$ MR 58.90; Found M 193.7; 189.3; Calculated M 198.

Found %: C 72.38; 72.38. H 10.63; 10.61;
Calculated %: C 72.72; H 11.11 $C_{12}H_{22}O_2$.

The analytical data correspond to tert-butylmethylethylethynyl acetal.]

The acetal is a colorless liquid with an ethereal odor; it turns yellow when kept and gives a characteristic white precipitate with an ammoniacal solution of silver nitrate. The acetaldehyde content of the acetal was determined

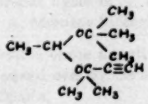
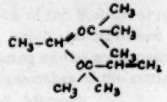
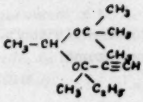
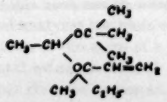
* Senior assistant Z. S. Volkova participated in the experimental work.

by the bisulfite method.

Found acetaldehyde 94, 83; 93, 72% of the theoretical.

TABLE 1

Characteristics of the prepared olefinic and acetylenic acetals

Number	Formula	B.p. in °C °C. (p in mm mercury)	d_4^{20}	n_D^{20}	MR Found	MR Calc-ulated	M Found	M Calc-ulated	%C Found	%C Calc-ulated	%H Found	%H Calc-ulated	Yield, in %
1		68-69 (16)	0.8692	1.4264	54.280	54.282	183.8	184.5 184.0	72.16	71.97 71.73	10.72	10.73 10.87	72.5
2		55 (6)	0.8532	1.4256	55.810	55.817	179.5	184.8 186.0	70.42	70.60 70.96	11.58	11.66 11.18	81.0
3		88-89 (13)	0.8694	1.4290	58.71	58.90	193.6	189.3 198.0	72.38	72.38 72.72	10.63	10.61 11.11	60.6
4		79-81 (12)	0.8540	1.4260	60.01	60.435	194.6	198.3 200.0	72.15	72.19 72.00	12.30	12.59 12.00	74.0

Reaction by the above-described procedure of vinyl-tert-butyl ether with methylethylvinyl carbinol and with dimethylethynyl- and vinyl carbinols in presence of a trace of 30% hydrochloric acid gave the corresponding acetylenic and olefinic acetals (see Table). The acetylenic acetals give a white precipitate with an ammoniacal solution of $AgNO_3$; the olefinic acetals do not give a precipitate, but they decolorize a weak solution of $KMnO_4$ and bromine water.

SUMMARY

1. A simple method is given for preparation of tertiary acetylenic and olefinic acetals containing tertiary butyl radicals; their properties are studied.

2. Dimethylethynyl(vinyl)- and methylethylethynyl(vinyl)-tert-butyl acetals were prepared.

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Received March 23, 1954

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* T.p. = C. B. Translation pagination.

CHRONICLE

THE HUNDREDTH ANNIVERSARY OF THE BIRTH OF ACADEMICIAN N. A. MOROZOV

June 8, 1954 marked the passage of 100 years since the birth of the celebrated savant-encyclopedist and outstanding chemist, one of the earliest revolutionists, Nikolai Aleksandrovich Morozov. His memorial, executed by the sculptor Prof. G. M. Motovilov was unveiled on this day in the birthplace of N. A. Morozov, at Bork in the Yaroslav Oblast. A bronze figure of N. A. Morozov seated on a stump with a book in his hand, was erected in the park of the["Borok"] N. A. Morozov Biological Research Station of the Academy of Sciences of the USSR.

An open session of the scientific council of the biological research station preceded the unveiling of the memorial and was presided over by the Academic Secretary of the Division of Biological Sciences of the Academy of Sciences, A. I. Oparin.

The director of the biological research station, Doctor I. D. Papanin, recounted the history of the biological research station, which was organized on the initiative of N. A. Morozov, and described its routine functions which have a close bearing on the great national-economic and scientific problems of Soviet hydrobiology. The growth and the fruitful researches of the station are a worthy memorial to the distinguished scientist and loyal son of the fatherland– N. A. Morozov.

The address on the life and activity of N. A. Morozov was given by candidate of historical sciences Sh. M. Levin (leningrad Division of the Institute of History of the Academy of Sciences USSR). He presented the main stages in the bright career of N. A. Morozov against the background of the despotic monarchical regime and the rise of the revolutionary movement. During nearly 30 years' solitary confinement in the Petropavlovsk and Shlisselburg fortresses, N. A. Morozov was able to make a profound study of various sciences and to carry out outstanding scientific researches.

Cand. Levin was followed by Acad. S. I. Volfkovich who reported on Morozov's researches in the field of natural science and in particular in chemistry. The reporter mentioned the outstanding importance of Morozov's work on "The periodic system of the structure of matter" which he wrote during many years of incarceration in the Shlisselburg fortress. In this book and in a series of other publications Morozov develops the theme of the complex structure of atoms and analyzes the basis of the periodic law of the chemical elements. He vigorously asserted the possibility of breakdown of the atom at a time when the majority of chemists regarded such a possibility as unreal and when experimental evidence for such a process was still lacking. Even at the end of the 19th century N. A. Morozov suggested that the most important problem of chemistry would by the "synthesis of elements". He considered that the chemical elements pass through an evolutionary process in the infinite development of the universe. He wrote: "What was a fantastic dream of the ancient alchemists may soon become a normal achievement of science". More than 50 years ago N. A. Morozov daringly and confidently advocated the theory of the complex structure of atoms, of the transmutability of elements, of the artificial preparation of radioactive elements, of the unusual stores of intraatomic energy. Reviving an idea of Dumas, N. A. Morozov advanced a periodic system of organic compounds ("carbohydride" radicals). At the start of the 20th century Morozov proposed the hypothesis that new stars are born by explosion of old stars due to decomposition of atoms of radioactive matter. Today this previously controversial hypothesis is accepted in slightly modified form by wide circles of astronomers and physicists.

S. I. Volfkovich later drew attention to a series of other notable ideas and discoveries of Morozov in various fields of science and indicated the need for deep and many-sided study of the rich literary works of Morozov.

The final speaker was Academician A. I. Oparin who pointed to the great importance of the studies in progress at the N. A. Morozov "Borok" Biological Research Station on hydrobiology, ichthyology, ornithology, hydrochemistry and other sciences. These researches are of importance not only locally but for the Union in general, particularly for clarification of the problems associated with the tremendous hydrotechnical developments in the USSR.

At the conclusion of the open session of the scientific council, at which were present Moscow representatives of the Academy of Sciences of the USSR, of societies from the oblasts and raions, as well as delegates of the Leningrad scientific institutes at which Morozov worked, the memorial was unveiled. The memorial commissioned by the Presidium of the Academy of Sciences was unveiled by Academician A. I. Oparin.

At the foot of the memorial were placed wreaths from the Presidium of the Academy of Sciences of the USSR, from the Division of Chemical Sciences of the Academy of Sciences of the USSR, from the "Borok" Biological Research Station, from the Leningrad V. F. Lesgaft Institute, and others. Also present at the unveiling of the memorial were representatives of local collective and state farms, and numerous young people.

DETERMINATION OF THE CRYSTALLIZATION COEFFICIENTS FOR THE DISTRIBUTION OF RADIUM BETWEEN SALT MELTS AND CRYSTALS OF BARIUM OR LEAD CHLORIDE

V. R. Klokman, A. A. Melnikova, and N. I. Uryupina

One of us, with Khlopin, has previously investigated the distribution of radium between a salt melt and crystals of a salt isomorphous with the corresponding radium salt [1].

It was found that, when a solid phase separates from the melt, the distribution of the microcomponent between the liquid and the solid phases proceeds, as it does in solutions, in accordance with Khlopin's law. In the systems examined - in which the solid phases were crystals of calcium, strontium, barium, and lead nitrates, and lead sulfate - the crystallization coefficient $\underline{D}$ (a measure of the enrichment of the separating crystals in the microcomponent, as compared with the salt remaining in the solution) was found to be constant, irrespective of the amount of solid phase that separated.

The values of the crystallization coefficients for the distribution of radium between salt melts and crystals in these systems are given in Table 1.

TABLE 1

System	D
$Ca(NO_3)_2-Ra(NO_3)_2-NaNO_3$	1.00
$Sr(NO_3)_2-Ra(NO_3)_2-KNO_3$	0.43
$Ba(NO_3)_2-Ra(NO_3)_2-NaNO_3$	0.45
$Pb(NO_3)_2-Ra(NO_3)_2-NaNO_3$	1.00
$PbSO_4-RaSO_4-Li_2SO_4$	1.08

It will be seen from Table 1 that in all of the systems that have been studied the crystallization coefficient $\underline{D}$ is either less than or equal to unity. This indicates that either enrichment in radium occurs in the liquid phase, or the radium is evenly distributed between the two phases. This is the reverse from what has generally been observed when crystallization occurs from a solution: for most salts the crystals are enriched in the microcomponent, even at a temperature of about 100° [2].

It was of interest to determine whether the distribution of the microcomponent in this way during the separation of the solid phase from a melt is the normal behavior or is merely characteristic of these particular salts. We therefore decided to continue this line of investigation and to determine the crystallization coefficients for the distribution of radium between salt melts and crystals of barium or lead chloride.

We selected barium chloride as a macrocomponent because in its crystallization from solution, even at about 100°, the crystals that separate are about twice as rich in radium as the salt remaining in solution ($\underline{D}$ =2.11 at 104.1°). Also, for barium chloride a suitable binary system can be found, i.e. one in which the components form no chemical compounds or solid solutions and in which the eutectic occurs at a relatively low temperature. As regards lead chloride, it is known that the radioactive lead isotopes (ThB and RaD) are coprecipitated with barium chloride and with radium chloride crystals when these separate from solution [3], so that these salts are isomorphous.

However, the coprecipitation of radium with lead chloride during the crystallization of the latter from solution has not been observed, but it is known that at high temperatures barium and lead chlorides form a continuous series of mixed crystals [4]. It was, therefore, of interest to determine the behavior of radium during the crystallization of lead chloride from a melt, since it would be expected, by analogy with barium, that under these conditions radium would also be coprecipitated with lead chloride, it being assumed that the close similarity in the properties of radium and barium is retained at high temperatures.

EXPERIMENTAL

The experimental procedure applied in the determination of the crystallization coefficients of radium has already been described in detail [1].

I. Determination of the Crystallization Coefficient for the Distribution of Radium between the Melt and Barium Chloride Crystals in the System $BaCl_2-LiCl$

The distribution of radium between melt and barium chloride crystals was studied in the binary system $BaCl_2-LiCl$, which has a eutectic at a relatively low temperature (510° according to Sandonnini) and gives melting point curves that correspond to the crystallization of the pure components.

The salts used in our experiments were first purified and dehydrated. Barium chloride was recrystallized and then dehydrated by drying it to constant weight at 120-125°. The lithium chloride contained a small amount of iron

impurity, and was therefore purified by treatment with ammonia, which precipitated ferric hydroxide. It was not possible to dehydrate lithium chloride by simple drying, since hydrolysis would occur.

According to the literature [5], anhydrous lithium chloride can be prepared either by the evaporation of a solution of lithium chloride to dryness in a current of hydrogen chloride, or by addition of ammonium chloride to an evaporating solution of the salt and heating of the dry residue, when the ammonium chloride is decomposed into ammonia and hydrogen chloride. We used the second method. The lithium chloride solution was filtered from the ferric hydroxide, and an equivalent amount of ammonium chloride was added. The solution was evaporated to dryness in an air bath, and the residue was then heated in a loosely covered platinum dish to remove ammonium chloride. At first, the residue was heated cautiously in order to remove residual water; it was then heated more strongly (decomposition of ammonium chloride into ammonia and ammonium chloride occurs at 335°). After removal of ammonium chloride the salt formed a white spongy mass, which was readily loosened from the walls of the dish.

As a check on the purity of the lithium chloride its melting point was determined and found to be 608°. The values given in the literature by various authors range from 602° to 614° [6]. The anhydrous salt was kept in a carefully sealed jar in a desiccator. All operations with lithium chloride were performed as quickly as possible, and the weights of samples were determined by the difference method.

The fusion of mixtures of barium chloride and lithium chloride for the determination of the melting curve of the system and for the distribution experiments was carried out in a porcelain crucible in an electric crucible furnace. The temperature of the melt was determined with the aid of a thermocouple of platinum and platinum-rhodium, which was graduated without a sheath at the freezing points of various salts.

On our fusion diagram of the binary system $BaCl_2$–LiCl the melting point of the eutectic is 510°, and the eutectic composition is 37.5 mole % $BaCl_2$ and 62.5 mole % LiCl. Our results are in good agreement with those of Sandonnini [7], who gives the eutectic melting point as 510° and the composition as 35 mole % $BaCl_2$ and 65 mole % LiCl. The determination of the radium contents of test samples of the melt taken before and after the separation of the solid phase was carried out by the emanation method.

In the determination of the crystallization coefficient for the distribution of radium between the melt and barium chloride crystals, nine experiments were carried out. Solid phase was allowed to separate from the saturated melt over the temperature range 710–522°. The results are given in Table 2.

TABLE 2

Distribution of Radium between the Melt and $BaCl_2$ Crystals in the Binary System $BaCl_2$–LiCl

Expt. No.	Amount of $BaCl_2$ separated as solid phase (%)	Amount of Ra separated in solid phase (%)	D
1	7.7	7.9	1.03
2	18.6	18.6	1.02
3	24.8	25.6	1.04
4	31.6	29.6	0.91
5	36.7	39.8	1.14
6	37.7	35.5	0.91
7	39.6	41.4	1.08
8	45.4	44.4	1.06
9	56.8	58.0	1.05
Mean			1.03 ± 0.05

It will be seen from Table 2 that, although there is a sevenfold variation in the amount of solid phase separated, the crystallization coefficient D remains constant at 1.03. These results indicate that in this system, as in all of the previous systems that we have studied, no enrichment of the solid phase in radium occurs when radium becomes distributed between the melt and the crystals of a salt that is isomorphous with the corresponding radium salt.

II. Determination of the Crystallization Coefficient for the Distribution of Radium between the Melt and Lead Chloride Crystals in the System $PbCl_2$ – NaCl

We have determined the crystallization coefficient for the distribution of radium between the melt and lead chloride crystals in the binary system $PbCl_2$–NaCl, which, according to the literature [8], has a simple eutectic, melting point 411°, and composition 27 mole% NaCl, 73 mole% $PbCl_2$.

Under the action of light and when heated in air lead chloride decomposes with formation of the oxychloride. The well dried salt, however, can even be sublimed without decomposition in an inert atmosphere. Recrystallized lead chloride was therefore dried, first by exposure to the atmosphere in the dark, and then, again in the dark, over phosphoric oxide in a vacuum desiccator. Also, immediately before the experiment, the lead chloride and sodium chloride were dried for some time in a crucible furnace at about 300°, the lead chloride being treated in an atmosphere of carbon dioxide.

The experiments for the determination of the melting diagram of the system and for the determination of

the radium crystallization coefficient were also carried out in an inert atmosphere. Melts produced under these conditions were transparent and of a light yellow color, which indicated absence of decomposition.

In this work we again used procelain crucibles, since it is not advisable to keep molten lead chloride in contact with platinum for a long time. Although lead chloride sublimes when heated, it was found by a special experiment that the losses from this source comprised a negligible part of the lead chloride taken for the determinations.

Our melting curve for the system $PbCl_2$–NaCl has a eutectic having a melting point of 409° and a composition of 70.7 mole % $PbCl_2$ and 29.3 mole % NaCl. The results of the experiments on the determination of the crystallization coefficient for the distribution of radium between the melt and lead chloride crystals are given in Table 3.

TABLE 3

Distribution of Radium between the Melt and $PbCl_2$ Crystals in the Binary System $PbCl_2$–NaCl

Expt. No.	Amount of $PbCl_2$ separated as solid phase	Amount of Ra separated in the solid phase (%)	D
1	30.0	26.2	0.83
2	42.5	40.4	0.91
3	44.6	43.3	0.95
4	51.5	48.4	0.88
5	52.3	50.3	0.92
6	61.7	59.4	0.90
7	62.4	57.7	0.82
8	63.0	59.5	0.86
9	65.7	61.3	0.82
10	69.0	65.8	0.87
11	78.2	74.0	0.79

Mean 0.85 ± 0.04

TABLE 4

Values of the Crystallization Coefficient of Radium for various Concentrations of Radium in the Original Melt

Expt. No.	Ra Concentration in the original melt (g of Ra per gram of melt)	D
1	$2.0 \cdot 10^{-9}$	0.81
2	$8.3 \cdot 10^{-8}$	0.91
3	$1.1 \cdot 10^{-7}$	0.85
4	$2.1 \cdot 10^{-6}$*	0.91
5	$1.9 \cdot 10^{-2}$	0.93

Mean 0.88 ± 0.04

* Increase in the concentration of the microcomponent was produced as a result of the addition of the corresponding amount of barium

In this series of experiments the solid phase was allowed to separate from the saturated melt over the temperature range 490-440°. Altogether, eleven determinations were made of the crystallization coefficient for the distribution of radium between the melt and $PbCl_2$ crystals. The crystallization coefficient D remained constant while the amount of separated solid phase varied by a factor of 2.5; its numerical value was 0.85.

Unlike the crystallization coefficient for the distribution of radium between a salt melt and lead nitrate or sulfate crystals (which has the value of unity), the crystallization coefficient in the present system is less than unity, so that again there is no enrichment of the solid phase in radium.

We carried out a second series of experiments for this system. In these we determined the crystallization coefficients of radium for various concentrations of radium in the original melt. As will be seen from Table 4, a change by a factor of several powers of ten in the radium concentration in the original melt has no effect on the value of the crystallization coefficient D.

In 1950 Khlopin formulated the following rule [9]: "If the distribution of a microcomponent (radioelement) between a solid crystalline phase and a solution is strictly in accord with the law for the distribution of a substance between two immiscible solvents and the crystallization coefficient D remains constant while the concentration of the substance being distributed varies over a wide range (by a factor of several powers of ten), then it may be considered to be proved that the Mitscherlich law can be extended to the given pair of substances, i.e. that the macro- and microcomponents are similar in chemical composition and molecular structure".

The constancy of the values of the crystallization coefficients that we have obtained for various concentrations of radium in the original solution in experiments on the distribution of radium between the melt and $PbCl_2$ crystals indicates, according to Khlopin's rule, that radium chloride crystallizes from the melt as the anhydrous chloride, isomorphous to lead chloride, i.e. behaves under these conditions as barium chloride does.

SUMMARY

1. The crystallization coefficients have been determined for the distribution of radium between a salt melt and

and barium chloride crystals and between a salt melt and lead chloride crystals.

2. It has been shown that in these two systems, as in previously studied systems in which radium is distributed between the melt and salts isomorphous with the corresponding radium salts, no enrichment of the solid phase in radium occurs.

3. It has been shown that the closeness in chemical properties of radium and barium is preserved at high temperatures.

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Received February 12, 1954

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KINETICS OF THE OXIDATION OF SIMPLE UNSATURATED HYDROCARBONS IN THE PRESENCE OF VANADIUM CONTACT CATALYSTS

L. Ya. Margolis, E. P. Malyarova, and S. Z. Roginsky

In the previous investigations [1] the use of labeled carbon (C^{14}) has enabled us to establish the main directions of reaction in the oxidation of ethylene and propene in presence of vanadium catalysts. The isotopic composition of the products showed that the process by which part of the carbon monoxide and dioxide was formed from the hydrocarbon was independent of that leading to the formation of acetaldehyde and ethylene oxide, and that these last substances could not be the main intermediate products in the destructive oxidation of the hydrocarbons. A comparative study by Andrianova and Roginsky [2] of the oxidation of propene and oxygen-containing substances (aldehydes and acids) over vanadium catalysts has shown that the low yields of aldehydes can be explained by their instability under the conditions of the experiment.

EXPERIMENTAL

The kinetics of the oxidation of ethylene and propene in mixtures of these hydrocarbons with air was studied under dynamic conditions at atmospheric pressure. We have determined the conditions required for the maintenance of isothermal conditions in investigations on the destructive oxidation of hydrocarbons [3]. The reaction products were analyzed as follows:

a) Organic acids were determined by titration to phenolphthalein with 0,01 N KOH.

b) Aldehydes were determined by the hydroxylamine method. In some cases determinations were made also of the proportions of acetaldehyde and formaldehyde by a polarographic method.

c) Gaseous products were analyzed for their contents of CO_2, CO, O_2, H_2, and hydrocarbons in the VTI gas analysis apparatus.

The kinetics of the oxidation of the hydrocarbons and certain of their reaction products (acetaldehyde and carbon monoxide) were studied also under static conditions at pressures of the order of 0,5 mm Hg. In these experiments aldehyde was separated by freezing it out in a trap immersed in a cryostat containing solid propyl alcohol (−126°), and carbon dioxide was absorbed with solid caustic potash. Carbon monoxide was mixed with oxygen and the mixture was ignited with an incandescent platinum wire; the resulting carbon dioxide was frozen out in a trap at the temperature of liquid nitrogen.

Catalyst

Ammonium vanadate was applied from solution to active silica having a specific surface of 300 sq. m per gram. The product was dried, and the ammonium vanadate was converted into V_2O_5 at 400°. Activation in a current of a nitrogen-hydrocarbon mixture yielded a catalyst which was found by X-ray analysis to contain a mixture of vanadium pentoxide and tetroxide. In the experiments carried out in the static apparatus, separate studies were made of the catalytic effects of pure vanadium pentoxide and pure vanadium tetroxide without carriers.

The experiments in the dynamic apparatus were carried out for 30 minutes at the selected temperature, and a fresh sample of catalyst was taken for each experiment. This procedure ensured good reproducibility of results. Before oxidation under static conditions, the catalyst was activated at 450°. Sorption of oxygen was then carried out at the same temperature and at a pressure of 2 mm Hg, after which the temperature was lowered and the excess of oxygen was pumped off.

Kinetics of the Oxidation of Propene over Vanadium Catalysts

The products of the oxidation of propene with oxygen or air in presence of vanadium catalysts include aldehydes, acids, carbon monoxide and dioxide, hydrogen, methane, and water. According to Tikhomirova's results [4], in the oxidation of ethylene the carbon monoxide content of the gas is twice as high as the carbon dioxide content. The only aldehyde present is formaldehyde, without acetaldehyde impuritie. Pigulevsky and Yarzhemskaya [5] showed that in the oxidation of propene the formation of 1 liter of gaseous aldehydes was accompanied by the formation of 0,1 liter of acids, 1 liter of carbon dioxide, and 1,8 liter of carbon monoxide, i.e. the ratio of CO to CO_2 was again close to two. There was more acetaldehyde than formaldehyde in the reaction products, and no propylene oxide could be detected.

was more acetaldehyde than formaldehyde in the reaction products, and no propylene oxide could be detected.

The composition of the oxidation products of hydrocarbons depends greatly on the concentrations of the starting materials. Isotope tracer experiments show that the process proceeds in several directions simultaneously. Each of these transformations is made up of a number of stages in which ordinary stable molecules and also labile forms (radicals, atoms, and ions) can take part. Confining the analysis of products to stable molecules, we may distinguish primary and secondary products for each direction of reaction.

The following processes have been detected with the aid of molecules labeled with C^{14}:

1. Formation of aldehydes with the possibility a) of subsequent decomposition with generation of carbon monoxide, b) oxidation to carbon dioxide, and c) oxidation to carboxylic acids (which are probably formed also without intermediate formation of aldehydes).

2. Oxidation of olefin oxides, followed by isomerization, decomposition, and oxidation of these.

3. Oxidation to carbon monoxide and dioxide without intermediate formation of aldehydes and olefin oxides, the probable intermediate being of the peroxide type. The oxidation of hydrocarbons via olefin oxides has been studied to a less extent owing to the high reactivities of the latter, and we shall confine ourselves to the analysis of the kinetics of reactions characterizing the first and third processes.

In order to determine order and rate constants for each of the component reactions: a) the contents of propene and oxygen in the reaction mixture were each varied from 4 to 27%, while maintaining the ratio of the concentrations constant; b) the content of oxygen was varied (2-14%) at a constant hydrocarbon concentration (4%).

Tables 1, 2, and 3 give the rate constants, calculated for zero- and first-order reactions, for the formation of aldehydes, carbon dioxide, and carbon monoxide respectively from propene.

For these three reactions the rate constants calculated from the zero-order equation increase as the concentrations of propene and oxygen increase. The reaction must therefore be of a higher order. When the concentrations of propene and oxygen are increased by a factor of 6-7, the rate constants calculated from the first-order equation remain practically constant, which indicates the applicability of this equation. Our calculations from the data of Bretton, Shen-Wu-Wan, and Dodge [6] (Table 4) on the oxidation of isobutene over V_2O_5 are in accord with our data on the oxidation of propene. Table 5 gives the rate constants with respect to oxygen for these reactions.

TABLE 1

Rate Constants for the Oxidation of Propene to Aldehydes

No.	Initial concentration of C_3H_6, c_0	Initial concentration of oxygen, c_0'	Zero-order constant, k_0	First-order constant, k_1	Notes
1	2	2.4	0.3	0.070	The oxidation experiments were carried out with simultaneous variation in the concentrations of the two reactants, and the reaction order has an overall value for $(O_2 + C_3H_6)$
2	4	4.0	0.5	0.068	
3	6	6.0	0.8	0.067	
4	8	8.0	1.28	0.065	
5	10	10.0	1.80	0.070	
6	12	12.0	2.2	0.070	
			Mean	0.068	

A sevenfold increase in the concentration of oxygen in the reaction mixture at a constant concentration of propene did not affect the rate constants for the reaction calculated from the first-order equation.

A comparison of Tables 1-5 shows that the first-order kinetics are determined by the oxygen, there being almost no effect ascribable to the concentration of hydrocarbon. The kinetic equations for the formation of aldehydes, carbon dioxide, and carbon monoxide from propene can therefore be written as follows:

$$1.\ \frac{d[ald]}{dt} = k_1[C_3H_6]^0[O_2]^1.$$

$$2.\ \frac{d[CO_2]}{dt} = k_1'[C_3H_6]^0[O_2]^1.$$

$$3.\ \frac{d[CO]}{dt} = k_1''[C_3H_6]^0[O_2]^1.$$

Fig. 1 shows the dependence of the logarithms of the rate constants for the formation of aldehydes, CO_2, and

CO from propene on 1/T. It will be seen that the relation between the rate constants and temperature is in accord with the Arrhenius law. The activation energies E are given in Table 6. Apart from our own results, Table 6 and Fig. 1 include data calculated from the results of Tikhomirova on the oxidation of ethylene and Bretton, Shen-Wu-Wan, and Dodge on the oxidation of isobutene. It is noteworthy in Table 6 that the activation energies for the formation of carbon dioxide are high and are equal for ethylene and propene. On the other hand, the activation energies for the formation of aldehydes from propene and isobutene are very low, but are again almost equal.

TABLE 2

Rate Constants for the Oxidation of Propene to CO_2

No.	Initial concentration of C_3H_6, c_0	Initial concentration of oxygen, c'_0	Zero-order constant, k_0	First-order constant, k_1	Notes
1	2	2.4	0.28	0.040	Order of reaction has an overall value for $(C_3H_6 + O_2)$
2	4	4.0	0.45	0.054	
3	6	6.0	0.70	0.054	
4	8	8.0	0.90	0.054	
5	10	10.0	1.1	0.054	
6	12	12.0	1.25	0.054	
			Mean	0.0515	

TABLE 3

Rate Constants for the Oxidation of Propene to CO

No.	Initial concentration of C_3H_6, c_0	Initial concentration of oxygen, c'_0	Zero-order constant, k_0	First-order constant, k_1	Notes
1	2	2.4	0.12	0.036	Order of reaction has an overall value for $(C_3H_6 + O_2)$
2	4	4.0	0.22	0.036	
3	6	6.0	0.52	0.038	
4	8	8.0	0.76	0.040	
5	10	10.0	0.96	0.040	
6	12	12.0	1.10	0.040	
7	14	14.0	1.20	0.038	
			Mean	0.038	

TABLE 4

Rate Constants for the Oxidation of Isobutene to CO and CO_2 over V_2O_5 (calculated from data of Bretton, Shen-Wu-Wan, and Dodge) at 400°

No.	Initial concentration of isobutene, c_0	Time of contact (sec)	First-order rate constant for formation of CO	First-order rate constant for formation of CO_2	Notes
1	0.76	0.1	0.43	0.25	Order of reaction has an overall value for $(C_4H_8 + O_2)$
2	—	0.2	0.049	0.025	
3	—	0.3	0.049	0.029	
4	—	0.4	0.049	0.028	
5	—	0.5	0.049	0.025	
6	—	0.6	0.048	0.025	
7	—	0.8	0.047	0.023	
8	—	0.9	0.047	0.025	
9	—	1.1	0.048	0.025	
		Mean	0.048	0.025	

The low activation energies for the formation of aldehydes and carbon monoxide do not appear to be explicable on the assumption that these reactions occur in the diffusion or intermediate zone, since the absolute values of the rates of the reactions are lower than the rate of formation of carbon dioxide.

TABLE 5

Rate Constants with Respect to Oxygen for the Formation of Aldehydes, CO_2, and CO

No.	Initial concentration of propene c'_0	Initial concentration of oxygen c'_0	First-order rate constants for the formation of aldehydes*	for the formation of CO_2	for the formation of CO
1	4.0	2	0.070	0.098	0.036
2	—	4	0.068	0.10	0.036
3	—	6	0.069	0.11	0.038
4	—	8	—	0.11	0.040
5	—	10	—	0.12	0.040
6	—	12	—	0.12	0.040
7	—	14	—	0.12	0.038
		Mean	0.069	0.11	0.038

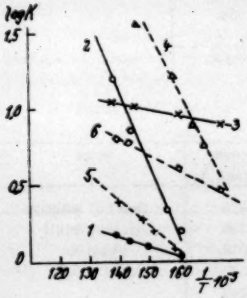

Fig. 1. Dependence of the logarithms of the rate constants for the formation of aldehydes, CO_2, and CO from various unsaturated hydrocarbons on 1/T: 1) aldehydes; 2) CO_2; 3) CO; 4) CO_2 from Tikhomirova's data; 5) CO from Bretton, Shen-Wu-Wan, and Dodge's data; 6) CO from Tikhomirova's data.

TABLE 6

Activation Energies E for the Formation of Aldehydes, Carbon Dioxide, and Carbon Monoxide from Various Hydrocarbons

Reaction	Hydrocarbon	Activation energy (kcal/mole)	Author
Formation of aldehydes	Propene	4	the present authors
Formation of CO_2	"	22	
Formation of CO	"	2	
Formation of CO_2	Ethylene	21	Tikhomirova [2]
Formation of CO	"	5	
Formation of CO	Isobutene	7	Bretton, Shen-Wu-Wan, and Dodge [6]
Formation of formaldehyde	"	5	

The main secondary reactions in the oxidation of hydrocarbons over vanadium catalysts are the decomposition and oxidation of aldehydes:

a) $RCHO \rightarrow CO + RH$;

b) $RCHO \xrightarrow{O_2} CO_2 + H_2O$

c) $2CO_2 + O_2 \rightarrow 2CO_2$

Over V_2O_5 at 300-400° carbon monoxide is oxidized to a comparatively small extent (10-15%). Over V_2O_4 the extent of the conversion into CO_2 is much greater (50-60%). These reactions were studied under static conditions over pure vanadium oxides V_2O_5 and V_2O_4.

Tables 7 and 8 give the values of the rate constants for the decomposition and oxidation of acetaldehyde over V_2O_5 and V_2O_4.

The constancy of the values for the rate constants for the decomposition of aldehydes indicates the applicability of a first-order equation, except to the very beginning of the reaction. The oxidation of acetaldehyde to CO_2 proceeds by a reaction of fractional order (0.2), except in the early stages.

Fig. 2 gives characteristic curves for the consumption of acetaldehyde and the formation of CO_2 over V_2O_5. The rapid reduction in the acetaldehyde concentration at the beginning of the reaction probably results from its rapid sorption on the surface of the catalyst and probably explains the anomalous initial rate constants for the de-

* The rate constants for the formation of aldehydes were calculated only as far as the maximum on the curve for the yield of aldehydes as a function of the oxygen concentration.

composition and oxidation of acetaldehyde. A study of the oxidation of acetaldehyde labeled with radiocarbon over V_2O_5 has shown that the aldehyde is taken up rapidly and firmly by the catalyst surface [1]. The noncorrespondence of the rate of formation of CO_2 and the rate of consumption of acetaldehyde may be a result of the slowness of the oxidation of the aldehyde adsorbed on the catalyst to CO_2.

TABLE 7

Rate Constants for the Decomposition of Acetaldehyde over V_2O_5 and V_2O_4 at 350°

Catalyst	Duration of reaction (min)	Initial concentration of CH_3CHO, c_0	Initial concentration of oxygen, c'_0	Zero-order rate constant, k_0	First-order rate constant k_1	Notes
V_2O_5	10	0.65	0.35	0.39	0.057	The value of k_1 for the first point is out of line with the others
	15			0.45	0.036	
	20			–	0.033	
	25			0.48	0.032	
	30			0.51	0.033	
	35			0.54	0.033	
	40			0.57	0.035	
			Mean (without first point)		0.034	
V_2O_4	10	0.64	0.34	–	0.041	The value of k_1 for the first point is out of line with the others
	15			–	0.030	
	20			–	0.025	
	25			–	0.024	
	30			–	0.025	
	35			–	0.024	
	40			–	0.025	
			Mean (without first point)		0.025	

TABLE 8

Rate Constants for the Oxidation of Acetaldehyde over V_2O_5

Duration of reaction (min)	Initial concentration of CH_3CHO, c_0	Initial concentration of oxygen, c'_0	Zero-order rate constant, k_0	First-order rate constant, k_1	Fractional-order rate constant, k_f
10	0.65	0.35	0.14	0.069	0.060
15			0.17	0.054	0.055
20			0.19	0.047	0.050
25			0.22	0.043	0.048
30			0.24	0.040	0.046
35			0.26	0.037	0.046
40			0.28	0.035	0.046
			Mean (without first and second points)		0.048

Hence, the kinetic orders and the activation energies have been found for primary and secondary reactions (Table 9) in the oxidation of propene over vanadium catalysts.

The closeness of the values of the activation energies for the formation and decomposition of aldehydes makes it impossible to regulate their accumulation among the reaction products by variations in temperature. The small differences found in the values of the activation energies for the formation of aldehydes, carbon monoxide, and carbon dioxide as we pass from one unsaturated hydrocarbon to another (ethylene, propene, isobutene) make it probable that the primary act of the oxidation is essentially the same in each case, leading finally to the cleavage of the molecule of the unsaturated hydrocarbon at the double bond. The difference in activation energy for the formation of carbon monoxide and the formation of carbon dioxide points to the independence of these two processes. Although the activation energies are so greatly different for these reactions, the reaction rates are similar. This makes it probable that there are great qualitative differences between the processes; thus, the formation of CO_2 may be a heterogeneous-

homogeneous reaction, whereas the formation of CO may be purely heterogeneous. Experiments on the oxidation of propene with heavy oxygen lend support to this suggestion [7]. The oxygen of the catalyst takes a leading part in the formation of carbon monoxide, but does not take such an important part in the formation of carbon dioxide. Also, different sites on the active surface may participate in these two independent reactions. Carbon monoxide, for example, may be formed on almost all of the sites on the catalyst surface, whereas the formation of CO_2 may occur on only a small fraction of them.

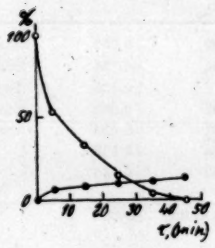

Fig. 2. Kinetic curves for the oxidation of acetaldehyde over V_2O_5 at 350°: 1) consumption of CH_3CHO; 2) formation of CO_2

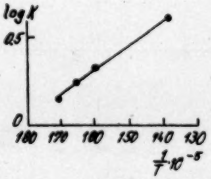

Fig. 3. Dependence of the logarithm of the rate constant for the decomposition of acetaldehyde over V_2O_4 on 1/T

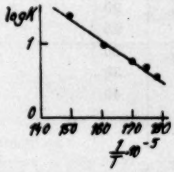

Fig. 4. Dependence of the logarithm of the rate constant for the oxidation of CO to CO_2 over V_2O_4 on 1/T

TABLE 9

Activation Energies for the Primary and Secondary Oxidation Reactions of Simple Unsaturated Hydrocarbons

No.	Reaction	Order of Reaction	Activation energy (kcal/mole)	Notes
1	Formation of aldehydes	First	4-5	Data on the oxidation of CO refer to V_2O_4
2	Formation of carbon dioxide	"	21-22	
3	Formation of carbon monoxide	"	2-7	
4	Decomposition of aldehydes	"	7	
5	Oxidation of aldehydes	Fractional (0.2)	5-6	
6	Oxidation of carbon monoxide	First	13	

The simplicity of the kinetics of the component reactions, as established in this work and their resemblance to the kinetics of the oxidation of ethylene to ethylene oxide in presence of silver make it necessary to examine critically the existing schemes for the catalytic process and to make refinements in the proposed mechanisms for the oxidation of simple unsaturated hydrocarbons.

SUMMARY

1. Aldehydes, carbon monoxide, and carbon dioxide, produced by the oxidation of propene over vanadium catalysts, are formed by first-order reactions.

2. The first-order kinetics of these reactions are determined by the oxygen, their rates being almost independent of the hydrocarbon concentration under the conditions studied.

3. The activation energies have been determined for the formation of aldehydes, carbon monoxide, and carbon dioxide from simple unsaturated hydrocarbons. The activation energy for the formation of carbon dioxide is much higher than the activation energies for the formation of carbon monoxide and of aldehydes, which are themselves very close in value.

4. The kinetics of the decomposition and oxidation of acetaldehyde in presence of vanadium catalysts have been studied, and the activation energies of these reactions have been determined.

5. The relative values of the activation energies for the vanadium-catalyzed primary and secondary oxidation reactions of the unsaturated hydrocarbons studied are such that it is impossible to effect a substantial increase in the aldehyde content of the reaction products by changes in the temperature of the process and the concentrations of the reactants.

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Received July 24, 1954

Institute of Physical Chemistry of the USSR
Academy of Sciences

* T.p. = C.B. Translation pagination.

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INVESTIGATION OF ELECTRODE PROCESSES OCCURRING DURING DEPOSITION AND DISSOLUTION OF SILVER IN CYANIDE SOLUTIONS

A. P. Popkov and A. T. Vagramyan

In the literature of electrochemistry there are many papers relating to investigations on electrode processes occurring during the deposition of metals in cyanide solutions [1]. A shortcoming of these papers lies in the fact that the explanations of the mechanism of the electrode processes and the character of the polarization are based solely on the basis of the forms and slopes of the curves for the dependence of polarization on current density. However, this relationship often does not give a complete picture of the processes occurring at the electrode under investigation, for it gives no idea at all of the changes in polarization with time. It is known that in the deposition and dissolution of metals polarization is not stable and changes with time [2], so that the forms and slopes of the polarization curves depend not only on the current density (other conditions remaining constant), but also on the rate at which the determination is made [3]. In a more detailed investigation of the electrode processes, therefore, it is necessary to study not only the dependence of polarization on current density, but also the change of polarization with time*. In the present investigation a study has been made of some processes occurring at a silver electrode polarized by alternating and intermittent currents.

EXPERIMENTAL

Experimental Procedure

The deposition and dissolution of silver was effected by alternating and intermittent currents obtained with the aid of a special commutator. A diagram of the commutator and the apparatus for recording changes in polarization is given in Fig. 1. The commutator consists essentially of an electromagnetic relay 1 and a switch-over disk 5. The electromagnetic relay effects the reversal of the polarizing current in the circuit II, and the frequency of the reversal and the time for which the current passes in the forward or reverse direction is regulated with the aid of the disk 5. The disk is made of insulating material and has a number of metallic contacts on its edge which can be connected to the metal ring 6. When the disc is rotated at a definite given speed, one of the contacts (for example, ab), in passing under the brush C, periodically makes and breaks the circuit feeding the electromagnetic coil 2 for a time proportional to the length of the metallic contact. When the circuit I is broken, the movable contacts 3 of the electromagnetic relay are pressed against the lower plates, as in Fig. 1, and the current flows in one direction. When the contact ab passes under the brush C, the circuit I is closed and the current, passing through the coil of the relay, switches the movable contacts 3 over on to the upper plates 4, and so changes the current in the electrolytic cell 13 over into the other direction. The durations of the positive and negative impulses can be varied over a wide range by increasing or diminishing the length of the contact ab and by changing the rate of rotation of the disk 5 with the aid of the gear box 7, which is connected to the electric motor 8. In order to obtain an intermittent current, i.e. a current that is interrupted periodically, the switch K is switched off, so that the current will pass in one direction for a time proportional to the length of the contact ab, and no current at all will pass for a time proportional to the insulated section bca.

Thus, with the aid of this commutator electrodes can be polarized both by alternating currents and by intermittent currents over a wide range of frequencies. As the processes investigated occupied such short periods of time, the polarization was recorded automatically with the aid of a cathode voltmeter 12 and a short-period (0.01 sec) mirror galvanometer 10. The record was produced with the light beam 11, which was reflected by the mirror of the galvanometer onto highly sensitive photographic film in the camera 9.

Experimental Results

With the aid of the above-described method, a study was made of the variation of polarization with time for a given constant value of the current**. Fig. 2 shows the cathode polarization curves for a current density of 5 ma/sq.cm in the solution: $K[Ag(CN)_2]$ – 0.25N; KCN – 0.38 at 18-20°.

*This sort of investigation is particularly necessary in various cases of nonstationary electrolysis; for example, when polarization is effected by alternating current [4], or when alternating current is superimposed on direct, etc.

**Constancy of polarizing current was attained by the inclusion in the circuit of a large resistance 17, much greater than the internal resistance of the electrolytic cell.

These curves show that, after the current has been switched on, the cathodic polarization rises comparatively slowly: after 0.14 second it is 76 mv (Curve 3). When the duration of electrolysis is increased to 0.84 second, the cathodic polarization attains 110 mv (Curve 2) and after 9.15 seconds it rises to 164 mv (Curve 1). The cathodic polarization comes to a stop after 2-3 minutes, and its absolute value attains 300 mv.

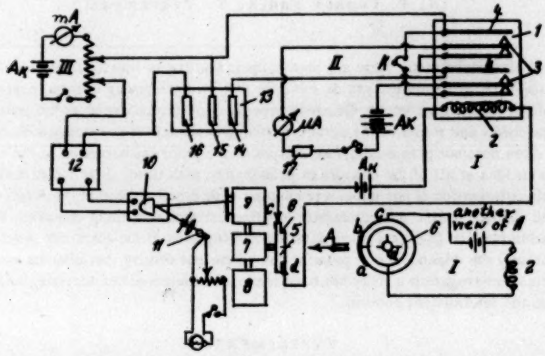

Fig. 1. Diagram of apparatus for the measurement of polarization during electrolysis with alternating and intermittent currents; 1) electromagnetic relay; 2) relay winding; 3) relay contacts; 4) upper plates; 5) Plexiglas disk; 6) metal ring; 7) gear box; 8) electric motor; 9) camera; 10) mirror galvanometer; 12) cathode voltmeter; 13) electrolytic cell; 15) investigated electrode; 16) auxiliary calomel electrode; 17) resistance

Fig. 3 shows curves for the change in anodic polarization with time, determined under the same conditions. When the current is applied to the electrode for 0.14 second, the anodic polarization attains 50 mv (Curve 3); when the duration of electrolysis is increased to 0.84 second, the polarization rises to 57 mv (Curve 2); and after 9.15 seconds it becomes 66 mv (Curve 1). Anodic polarization comes to a stop after 2-2.5 minutes and its value attains 85 mv. When the curves in Figures 2 and 3 are compared it will be seen that the absolute values of the anodic polarization are lower than those of the cathodic polarization. This is evidence of the great difficulty of the cathode process in comparison with the anode process at the same current density (5 ma/sq.cm).

Fig. 4 shows the curve for the change in the cathodic and anodic polarizations with time determined in the same solution during electrolysis with a symmetrically alternating current. Comparison of Curves 1 in Figures 2 and 3 with the curve in Fig. 4 shows that the absolute values of the anodic and cathodic polarizations fall considerably when alternating current is used. The explanation of this lowering of the polarization is that the impoverishment of the electrode surface layer during the separation of silver is succeeded by its enrichment during the dissolution of silver. As a result, both the cathodic and the anodic polarizations are lowered.

Fig. 5 shows polarization curves determined by the rapid method [5] in the same solution at the maximum current density (50 ma/sq.cm). Curve 1 was taken at a rate of 0.416 cm/sec. One period of this curve, i.e. the sum of the time for which the electrode acted as anode and the time for which it acted as cathode, was 30 seconds. Curve 2 was taken at a rate of 4.166 cm/sec, and the durations of the cathodic and the anodic polarizations were each three seconds. Curve 3 was taken at a rate of 12.5 cm/sec, and the duration of one period was one second. As will be seen from these curves, the absolute values of the cathodic and anodic polarizations and the form of the curves depend greatly on the rate at which the determinations were made. When they were made at a low rate (0.416 cm/sec), the anode curve had quite a different appearance, and differed from the cathode curve by the presence of characteristic "steps", the physical significance of which will be examined below.

Fig. 6 shows the variation of cathodic and anodic polarizations with time in electrolysis with alternating current of density 50 ma/sq.cm. The curve shows that the limiting value of the cathodic polarization is attained after 3 seconds and has the value of 0.75 v; at the same time vigorous evolution of hydrogen occurs. When the direction of

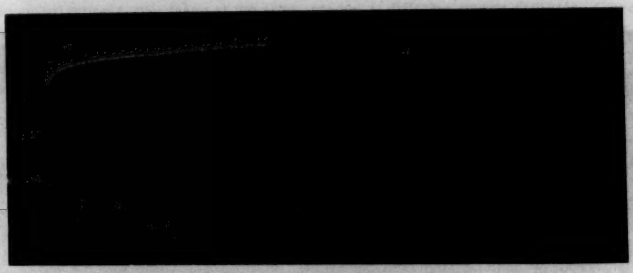

Fig. 2. Variation of cathodic polarization with time ("cek" = sec.)

Fig. 3. Variation of anodic polarization with time ("cek" = sec.)

Fig. 4. Variation of polarization with time during electrolysis with alternating current. ("sec" = sec.)

Fig. 5. Polarization curves taken by the rapid method at a maximum current density of 50 ma/sq. cm.

Fig. 6. Variation of polarization with time during electrolysis with alternating current.

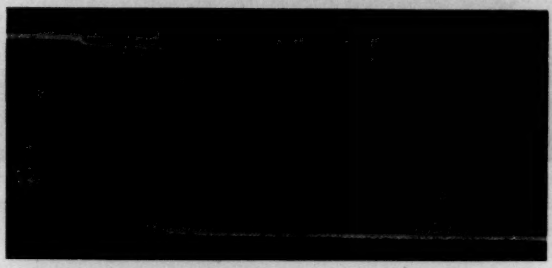

Fig. 7. Variation of anodic polarization with time.

the current is reversed, the passivation of the electrode is brought about in 2.15 seconds. The next reversal of current removes the anodic passivity, and the above-described process is repeated. When, however, the duration of deposition and dissolution of silver is diminished, conditions may be attained under which the cathodic and anodic polarizations cannot attain their limiting values.

Fig. 7 shows anodic-polarization curves taken at the same rate but at differing current densities. Curve 1 was taken at a current density of 10 ma/sq.cm, Curve 2 at 20 ma/sq.cm, and Curve 3 at 30 ma/sq.cm. On two of the curves there are characteristic plateaus. When the anodic polarization corresponds to the section Oa, the current is mainly consumed in dissolving silver with formation of complex cyanide ions. The point a corresponds to the beginning of passivation of the anode, i.e. the formation of a silver oxide film that prevents further dissolution:

$$2\,Ag + 2OH^- - 2e \rightleftarrows Ag_2O + H_2O$$

The plateau ab is generally found at a potential of 0.6 v relative to the potential of a silver electrode in the same solution. The length of ab diminishes as the current density increases, but the quantity of electricity spent in the formation of the oxide film remains almost constant and corresponds approximately to the formation of a monomolecular layer of silver oxide. The quantity of electricity depends only on the surface relief of the anode. At the point b the whole surface of the electrode is covered by an oxide film and there is a sharp rise in the anodic polarization, corresponding to further thickening of the oxide layer and separation of bubbles of oxygen.

Fig. 8 is the curve for the variation of anodic polarization with time during the dissolution of silver by means of an intermittent current. Over the section oc the electrode is polarized by a high-density current which renders the anode passive. At the point c the current is switched off, and section df corresponds to the variation of the potential of the electrode when there is no current. In the curve for the fall in polarization in absence of current there is a sudden check (section de) at the same potential as that at which silver oxide forms, and this corresponds to the dissolution of the oxide film in potassium cyanide with formation of a complex silver cyanide.

$$Ag_2O + 4KCH + H_2O \rightleftarrows 2KAg(CN)_2 + 2KOH$$

The further slow fall in the potential along the section ef results from the levelling out of the concentrations of complex silver ions in the layer in immediate contact with the electrode.

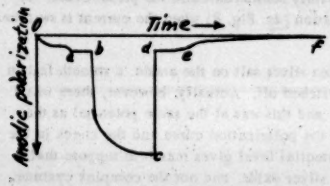

Fig. 8. Variation of anodic polarization with time during electrolysis with an intermittent current

Examination of the surface of the anode showed that at low current densities the silver dissolved with exposure of its structure. At high current density, when passivation of the anode occurred (Fig. 7, Curves 2 and 3), the surface of the silver was covered by a dark-colored oxide film; this had cracked in some places, and some of it had broken away as a result of internal strians and of mechanical disruption due to the separation of bubbles of oxygen. When the anode was polarized with an intermittent current, so that the oxide film was alternately formed and dissolved (Fig. 8), electrolytic polishing of the silver occurred.

DISCUSSION OF RESULTS

Cathodic polarization during the deposition of metals can be the result of the slowest stage of one of the following processes: 1) formation and growth of crystals on the cathode; 2) slow discharge of ions; 3) slow decomposition of complex ions; and 4) slow delivery of discharging ions to the cathode.

The curves given above, which were determined during the deposition of silver from cyanide solutions, cannot be explained by the slowness of the formation of crystals, for, as has been pointed out in a number of investigations [6], when the process is retarded by electrocrystallization, the polarization is high only at beginning of the process and falls as the crystals forming at the cathode grow. However, the polarization curves obtained (Figs. 2, 4 and 6) show exactly the opposite picture of the variation of polarization with time, indicating that cathodic polarization must be due to other causes.

Again, the observed polarization during the deposition of silver from cyanide solutions cannot be explained by the slowness with which the complex ions are dehydrated and discharged, for, if the discharge were slow, the polarization would not vary, i.e. its value would remain constant with time.

The nonvalidity of explanations of the polarization based on the slowness with which complex silver cyanide ions are decomposed has been demonstrated fairly conclusively in some previous papers [7]. We consider that the slow rise of polarization with time and the great reduction in its value in electrolysis with alternating current (Fig. 4) can be explained by a) the slowness with which the discharging ions are delivered to the electrode* (concentrational polarization); and b) the slowness with which the discharging ions [in particular $Ag(CN)_2^-$] penetrate into the electrical double layer, i.e. the slowness with which they are adsorbed and the slowness of the process of displacing other ions and particles situated at the cathode surface.

Since the rate of the electrochemical reaction is determined by the concentration of the discharging anions adsorbed on the surface of the cathode, a lowering of the polarization will be observed, both when the current is periodically switched on and off (Fig. 2), and when the direction of the current is reversed (Fig. 4). The polarization is lowered to a particularly great extent when the direction of the current is reversed, for in the cathodic impulse the electric field is directed against the adsorption forces.

The picture that we have described of the variation of polarization with time can be interpreted as a kind of concentrational polarization, although this concept would need to be extended somewhat in content and sense. This polarization differs from the usual concentrational polarization in that the migration of ions is in the reverse direction and the concentration of the discharging ions at the electrode surface depends on the rate of adsorption, i.e. on the rate at which they penetrate the electrical double layer and on the rate at which they can displace other ions and foreign species from the cathode surface.

An examination of the changes in anodic polarization with time indicates that this also is concentrational and the way in which the anodic polarization changes at low current densities is analogous to the behavior of cathodic polarization, as can be seen from the curves in Figures 2 and 3. The fact that the polarization occurring during the deposition of silver from cyanide solutions is concentrational makes it possible to deposit with an alternating current and to use high current densities, without reaching the limiting values. As a result it is possible to improve the quality of cathode deposits.

As indicated above, when the anode is polarized by high current densities, it becomes passive (Figures 5, 6 and 7). In the literature [8] the passivation of silver in cyanide solutions has often been explained by the supersaturation of the layer in contact with the anode with the silver complex salt and its precipitation on the electrode surface as a viscous, passivating film. We consider that this view is not fully substantiated in the present case, for it is impossible to explain, on its basis, the check in the fall in polarization (de, Fig. 8) when the current is switched off.

If the section ab corresponded to the crystallization of the complex silver salt on the anode, a smooth fall in potential with time should have been observed when the current was switched off. Actually, however, there was a check in the fall of the polarization when the current was switched off, and this was at the same potential as that at which the oxide was formed. The fact that the check in the rise of the polarization curve and the check in the fall of potential when the current was switched off were at the same potential level gives reason to suppose that the process occurring at the anode was the formation and dissolution of silver oxide, and not the complex cyanide.

It should be noted in conclusion that it is usual in the examination of the mechanism of electrode processes to study the dependence of the value of the polarization on the current density, without taking into account the changes of polarization with time, in spite of the fact that in some cases these changes are very important for the understanding of the kinetics of the processes.

SUMMARY

1. A simple method has been developed for the study of nonstationary electrode processes of short duration.

2. It has been shown that cathodic and anodic polarizations occurring during the deposition and dissolution of silver in cyanide solutions are essentially concentrational.

3. It has been shown that three sections can be distinguished in the curves for the variation with time of anodic polarization during electrolysis at high current densities, and that these correspond to the following processes: a) dissolution of silver with formation of complex cyanide ions; b) formation of a monomolecular layer of silver oxide on the electrode surface; and c) the further thickening of the oxide film and the evolution of free oxygen.

* The slow rise of the polarization with time cannot be explained by the charging current, since the current required for the charging of the electrical double layer is comparatively insignificant.

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Received April 3, 1954

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INTERHALOGEN COMPOUNDS AS COMPLEX- FORMERS*

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Interhalogen compounds, i.e. compounds formed by one halogen with another, have for the main part received little study. Until very recently the information appearing in the literature on the properties of these compounds with the possible exception of iodine chloride, has been meager and sporadic and has not afforded a sufficiently complete characterization of this peculiar group of inorganic compounds, which are of great interest, both theoretical and practical. In the last two decades some previously unknown halogen fluorides have been prepared, the physical and chemical properties of the interhalogen compounds have been investigated in greater detail, and new ways have been found for their practical application. This activity has been accompanied by increased interest in this group of inorganic compounds.

Many of the peculiarities of the interhalogen compounds are to be attributed to the fact that they are formed from atoms of elements belonging to the same group and subgroup of Mendeleev's periodic system. The halogen subgroup differs from most of the other subgroups of the periodic system in that its members fairly readily unite with each other in pairs - each of the four halogens with the remaining three - with formation of substances varying in stability.

Eleven interhalogen compounds are now known, and these may be divided into four groups - AB, AB_3, AB_5, and AB_7 - according to the numbers of the halogens, and also into three groups - either as the halides of chlorine, bromine, and iodine, or as the halogen fluorides, chlorides, and bromides - according to chemical composition. The classification of the interhalogen compounds is given in Table 1.

TABLE 1

Classification of Interhalogen Compounds

Main groups of interhalogen compounds	AB	AB_3	AB_5	AB_7
Chlorine fluorides	ClF	ClF_3	–	–
Bromine fluorides	BrF	BrF_3	BrF_5	–
Iodine fluorides	–	–	IF_5	IF_7
Bromine chlorides	BrCl	–	–	–
Iodine chlorides	ICl	ICl_3	–	–
Iodine bromides	IBr	–	–	–

Table 2 gives some of the physicochemical properties of the interhalogen compounds. The data in this table demonstrate the variety in the physicochemical properties of the interhalogen compounds (melting and boiling points, molecular state, conductivity, thermal stability), which is determined by the properties of the component halogens and valency state of the heavier halogen, the positively charged center of the molecule.

A discussion of the factors determining the physicochemical properties of the interhalogen compounds is outside the scope of this paper. We may remark, however, that, apart from the factors mentioned above (the chemical nature and valency states of the halogens), the molecular structure of the compounds and effects associated with the screening of the central atom are also of great importance. The effect of the last factor, which reduces intermolecular association, is reflected particularly clearly in the values of the melting points and boiling points.

An examination of the data in Tables 1 and 2 prompts questions relating to the causes of the low thermal stability or nonexistence of certain interhalogen compounds corresponding both to high and to low valence forms of the halogens. These questions are most difficult to answer for the lower types of interhalogen compounds, such as AB and AB_3, the stabilitites of which fall in the fluoride series in the order of chlorine, bromine, and iodine fluorides; in the series of bromine and iodine fluorides the stability increases as we pass from the lower (AB) to the higher forms (AB_5 and AB_7), and for iodine it has not been found possible to prepare the mono- and tri-fluorides IF and IF_3, while BrF_5, IF_5, and IF_7 are among the most stable of the interhalogen compounds. For the reasons given above we cannot discuss these and related matters here, but it may be pointed out that similar phenomena are known for the fluorides of elements in some of the other subgroups of the periodic table.

The interhalogen compounds, particularly those of type AB, show similarities to the halogens themselves in

* Paper read at a joint session of the Division of Physico-Mathematical, Chemical, and Geological Sciences of the Academy of Sciences of the Ukrainian SSR and the Division of Chemical Sciences of the Academy of Sciences of the USSR on May 11-13, 1954, in Lvov.

their physical and chemical properties, as pointed out long ago by D. I. Mendeleev when examining the properties of iodine chloride and trichloride [1].

TABLE 2

Some Physical Properties of Interhalogen Compounds

Formula	M.p. (°C)	B.p. (°C)	State at room temperature	Electrical conductivity at the melting point ($ohm^{-1} \cdot cm^{-1}$)	Trouton's constant	Density at the boiling point	Degree of dissociation in the vapor phase at 25° (%)
ClF	−155.6	−100.1	Gas		28	1.62	$1.2 \cdot 10^{-7}$
ClF_3	− 82.6	12	Gas	$3 \cdot 10^{-9}$ (at 0°)	20.8	1.8495	5.2 •
BrF	~−33	~20	Liquid		20.5(?)		Very high (complete at 50°)
BrF_3	8.8	127.6 ± 1	Liquid	$3.1 \cdot 10^{-3}$	25	2.51	Very low
BrF_5	61.3	40.5 ± 0.5	Liquid		23.7	2.41	Insignificant••
IF_5	9.6	98 ± 1.5	Liquid	$1.6 \cdot 10^{-5}$	27.2		Insignificant•••
IF_7	5−6	4.5	Gas		<26.4	2.80	Insignificant••••
BrCl	From about −66 to −54	Near to room temperature	Gas				21
ICl_α	27.2	100−102	Solid	$4.40 \cdot 10^{-3}$	26.7		0.38
ICl_β	13.9						
ICl_3	101 (at 16 atm)	Decomposes	Solid	$8.5 \cdot 10^{-3}$			complete
IBr	42	~166	Solid	$4.0 \cdot 10^{-4}$			8.8

• This value is that of the degree of association of ClF_3 at 1 atm.

•• Bromine pentafluoride is stable at least up to 460°.

••• Iodine pentafluoride begins to decompose only above 400°.

•••• Iodine heptafluoride is stable at least up to 500°.

The interhalogen compounds also show definite differences in chemical properties from the free halogens from which they are formed. These peculiarities are to be attributed to the polar character of their molecules and their relatively high polarizability, to the electropositive character of one of the component halogens, and to the electrolytic dissociation of many of them with the formation of positively and negatively charged halogen ions. These peculiarities of interhalogen compounds determine their high reactivity in various reactions•, including complex-forming reactions.

The principal chemical properties of interhalogen compounds are as follows:

1) They are powerful oxidizing agents for various inorganic and organic substances.

2) When they react with various inorganic substances - oxides, salts, and others - they form the corresponding simple or complex halides. These reactions, which often have very complicated mechanisms, are partially of an oxidation-reduction type.

3) Some interhalogen compounds (ICl, IBr, BrCl, and others) are able to add at multiple bonds in unsaturated organic compounds.

4) They are able to halogenate organic compounds (phenols, amines, etc.) by replacement of hydrogen by halogen.

5) They combine with nitrogenous and oxygenous organic bases, and similar compounds, with formation of complex compounds of the type:

•Chlorine fluorides, for example, are often more reactive than chlorine or fluorine separately.

$C_5H_5N \cdot ICl$[2,3]; $C_5H_5N \cdot 2ICl$[3]; $C_4H_8O_2 \cdot ICl$[4]; $C_4H_8O_2 \cdot IF_5$[5]; $C_5H_5N \cdot ICl_3$, $C_5H_{11}N \cdot ICl$[6,7]; etc.

6) They form complex (so-called double) halides with the halide of other elements, for example:

$KCl \cdot ICl$[8,9]; $PCl_5 \cdot ICl$[10,11]; $PBr_5 \cdot IBr$[12]; $BrF_3 \cdot KF$, $BrF \cdot SbF_5$[13]; $KF \cdot IF_5$[14].

Even this incomplete list of the types of chemical reactions that can be effected with the aid of interhalogen compounds will indicate the possible significance that this group of inorganic compounds can have in chemical practice, in particular the chemistry of complex compounds.

The nature of the solvent has a great effect on the behavior of interhalogen compounds in chemical reactions. The effect of the solvent is manifested in the following ways:

1. Solvation of interhalogen molecules, and the ions that they form, by the molecules of polar solvents.

2. Polarization of interhalogen molecules. Thus, the dipole moment of iodine chloride in the gaseous state is 0.65 D [15], and increases when the compound is dissolved in carbon tetrachloride or cyclohexane to 1.48 D[16]. The additional polarization of interhalogen molecules under the action of the solvent can lead to a considerable increase in the ionic character of the bond $Hal^I - Hal^{II}$.

3. Finally, the solvent may affect the way in which the interhalogen compound dissociates: not only does thermal dissociation occur with formation of halogen molecules, but also electrolytic dissociation. For iodine chloride the equilibria can be represented as follows:

$$I_2 + Cl_2 \rightleftarrows (ICl)_2 \rightleftarrows I^+ + ICl_2^- \rightleftarrows 2I^+ + 2Cl^-.$$

Increase in the polar character of the solvent (increase in dipole moment and, particularly, dielectric constant) will create, as a result of processes indicated above, conditions favorable for a shift in the equilibrium in the direction of an increase in the concentration of ions* in the solution. Such solutions, therefore, will conduct an electric current.

Interhalogen compounds are very interesting in their relation to the chemistry of complex compounds. Their intermediate state between nonpolar halogens and highly polar halides, their variety in composition and chemical properties, and their comparatively high polarizabilities create the possibility of studying well-defined manifestations of a very important factor in processes of complex formation, namely, the mutual polarization of the reaction components, as observed for complex compounds having a nonmetallic central atom. As is well known, complex compounds of this type have been prepared in smaller numbers and have been investigated to a much less extent than complexes in which the central atom is derived from a metal ion.

A comparative study of complex-forming reactions in which halogens or interhalogen compounds take part would also be of great interest. Until recently, however, only a few complex compounds formed by interhalogen compounds were known; their structures were obscure, and their place in the system of classification of complex compounds was uncertain.

The main object of this paper is the examination of these and other similar matters on the basis of data from the literature and the results of investigations carried out by the author with the collaboration of Kuzmenko Kuzyka, Kaganskaya, Shor, Abarbarchuk, and others at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR.

The complex compounds formed by interhalogen compounds may be devided broadly into two groups:

I. Addition compounds formed with nitrogenous, oxygenous, and similar organic bases (see above).

Complex compounds of this group include compounds that vary greatly in stability: from solvates of variable composition occurring in a state of dissociation in solution, through various intermediate forms, to highly stable complexes, which do not decompose even when heated above their melting points.

A study of these interhalogen complex compounds is of great interest also for the theory of solutions. In the more stable compounds of this type there is a coordinate link. Such a link may be formed when the interhalogen compound dissociates into ions owing to the polarization of its molecules by the solvent. The resulting positively charged halogen ions add as electron acceptors, to oxygen, nitrogen, or similar electron-donating atoms in the molecules of the organic base. This process results in the formation of complex cations of the onium type, for example

$$C_5H_5N: + I : Cl: \longrightarrow [C_5H_5N - I]^+ Cl^-$$

* solvated by solvent molecules

or

$$C_5H_5N{:} + I^+[ICl_2]^- \longrightarrow [C_5H_5N{-}I]^+[ICl_2]^-$$

This concept of the nature and structure of the ions yielded by such halogen and interhalogen complex compounds was advanced by us [17] with the object of explaining phenomena observed during the electrolysis of these compounds (or solutions of iodine halides ICl, IBr, and ICl_3 in polar organic solvents): both halogens - iodine and chlorine or iodine and bromine - were finally (when electrolysis was sufficiently prolonged) transferred to the anode•, although during electrolysis the ratio I/Cl or I/Br increased in the cathode department and diminished in the anode department. The molecules of the organic substance were transferred to the cathode.

On the basis of data in the literature and the results of the author and Muzyka, we have proposed the following scheme of the electrode processes:

a) Anode process: $2Cl^- - 2e = Cl_2$

b) Cathode process: $2[R{-}I]^+ + 2e = 2R + I_2$.

The iodine molecules liberated at the cathode undergo cathodic reduction, $I_2 + 2e \rightarrow 2I^-$, and the resulting iodide anions are then transferred to the anode. Hence, as shown by the author with Kaganskaya [9] and Muzyka [3] for the electrolysis of the systems $C_6H_5NO_2$–ICl and C_5H_5N–ICl, at first AgCl is deposited on the silver anode, but later also AgI is deposited.

The cathodic reduction of iodine during the electrolysis of aqueous and nonaqueous solutions of polyiodides has been proved by Shevchenko [18].

The formation of a coordinate link in molecular compounds formed by halogens and by interhalogen compounds with organic substances has been shown also in a series of investigations carried out at Leningrad University by Shukarev, Lilich, and others [19-20]. Lilich and Presnikova [22] made calculations, based on spectrophotometric measurements, of the equilibrium constants (stability constants) of molecular compounds formed by bromine, iodine, iodine chloride, and iodine bromide with dioxan and methanol. The thermal stabilities of these complexes increase in the order $Br_2 < I_2 < IBr < ICl$, i.e. in the order of increased asymmetry of the distribution of outer electrons in the halogen or interhalogen molecule. The stabilities of these molecular compounds increase also as the electron-donating properties of the organic "bases" increase••, for a given electron acceptor. The presence of a coordinate link in the compound $C_5H_5N \cdot ICl$ has been confirmed also by the work of Sheka [23], who established the formation of an equimolecular complex in the system C_5H_5N–ICl in chloroform solution on the basis of measurements of the departures of the values of dielectric constant and polarization in this system from their additive values.

An examination of the literature shows that the molecular compounds betweeen interhalogen compounds and organic substances are formed almost entirely by the addition of ICl, IBr, or, rarely, ICl_3 to various aliphatic, aromatic, and heterocylic amines. In view of this fact Fialkov and Muzyka have investigated the reaction of iodine chloride and bromide with amides, the molecules of which contain two different electron donors, the nitrogen atom and the oxygen atom:

Investigations in this field demand extensive application of methods of physicochemical analysis.

Two directions of development can be distinguished in the investigation of the chemistry of complex compounds. The first of these consists in the investigation of systems that for practical purposes are nonequilibrium systems, i.e. systems in which the position of equilibrium is almost completely displaced in the direction of the formation of stable complex compounds that may be separated, comparatively easily and at the same time almost quantitatively, from the system. Investigations on such complex compounds, e.g. platinum compounds, are characterized by the predominant use of preparative methods, i.e., the synthesis of the complex compound to prove that complex formation occurs, followed by the establishment of the composition, structure, and properties of the complex by the methods of chemical analysis and of physical chemistry.

The second of these directions consists in the investigation of systems in which comparatively unstable complex compounds are formed. In the investigation of these systems the method of physicochemical analysis, so brilliantly developed in our country by Kurnakov and his school, has acquired extreme importance.

• When silver anodes were used, a deposit of the corresponding silver halides was formed on their surfaces.

•• Compounds formed with dioxan are more stable than those formed with methanol.

Equilibrium systems, and the unstable complex compounds that are formed in them, are of considerable interest, partly because they are so common, and partly because they comprise an intermediate field between the systems that, for practical purposes, are nonequilibrium systems, and solutions. These systems include most of the systems in which complex compounds are formed between interhalogen compounds, in particular iodine halides, and organic bases of halides of other elements.

In the Complex Compounds Laboratory of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR, systems containing compounds of iodine halides, and, in fact, equilibrium systems in general, are investigated by a combination of several methods of physicochemical analysis in order to detect complex compounds and determine their compositions, and this is followed by the isolation (synthesis) of individual compounds and their investigation with the aid of chemical analysis and of physicochemical methods, including, when possible, electrochemical methods. The experience gained in our laboratory has shown that such a combination of methods of investigation enables complex compounds to be studied from all angles and enables us to obtain conclusive results concerning their presence, compositions, properties, and structures.

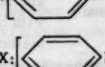
As a result of such investigation on systems consisting of iodine chloride and acetamide CH_3CONH_2 [24], benzamide $C_6H_5CONH_2$ [25], and NN-diethylbenzamide $C_6H_5CON(C_2H_5)_2$ [26], and also on the systems IBr–$C_6H_5CONH_2$ [27] and ICl–C_5H_5N [3], it was found possible to prepare a number of complex compounds not previously described in the literature, or to establish their formation in the liquid phase and determine some of their physicochemical properties and the nature of the ions present, etc.

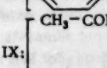
It was shown that in such systems complexes of four types are formed:

1. Compounds of the type $R \cdot IX$: $CH_3CONH_2 \cdot ICl$; $C_6H_5CONH_2 \cdot ICl$; $C_6H_5CONH_2 \cdot IBr$; $C_5H_5N \cdot ICl$; $C_5H_5N \cdot IBr$.
2. Compounds of the type $R \cdot 2IX$: $C_5H_5N \cdot 2ICl$.
3. Compounds of the type $2R \cdot IX$: $2CH_3CONH_2 \cdot ICl$.
4. Compounds of the type $(R \cdot IH)_2$: $(C_6H_5CONH_2 \cdot ICl)_2$.

On the basis of results obtained from the study of ion transfer and certain other data the following structures are suggested for complex compounds of these types:

1. For $R \cdot IX$: Cl; $[C_6H_5CONH_2 \cdot I]Br$.

2. For $R \cdot 2IX$:  $[ICl_2]$.

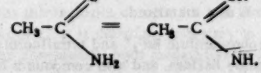
3. For $2R \cdot IX$:  Cl.

4. For $(R \cdot IX)_2$: $[ICl_2]$.

In compounds of the last two types the I^+ ion forms a covalent bond, as an electron acceptor, with one amide molecule, and a bond with the other molecule that probably results from polarization or Van der Waals interaction.

The structure of the cation $[(C_6H_5CONH_2)_2I]^+$ can be compared with that of the so-called "anomalous" ammonium salts, for example $[2NH_3 \cdot H]Cl$.

In considering the structure of compounds formed by iodine halides with amides we must remember that carboxylic amides can be represented by two tautomeric formulas, for example:



It was found that NN-diethylbenzamide $C_6H_5CON(C_2H_5)_2$, which cannot undergo tautomeric rearrangement, reacts with iodine chloride with formation of an equimolecular compound having similar properties to that of the

analogous compound derived from unsubstituted benzamide. We may infer from this that amides react with iodine chloride and iodine bromide in the first (amide) form of the two shown above. As regards the question of which electron donor - the nitrogen or the oxygen - participates in the link between the amide molecule and the I^+ ion, these investigations do not yet provide an answer.

II. The second group of complex compounds formed by interhalogen compounds contains addition compounds formed by bromine and iodine halides with the halides of other elements or the halides of complex inorganic or organic cations (see early part of paper).

Many of these complex compounds, which belong to the class of double halides, are considerably more stable than the original bromine and iodine halides. Also, they are so active chemically that they may be successfully applied for various purposes - for oxidation reactions, and for the halogenation, in particular fluorination, of inorganic and organic substances, etc.

The formation of complex compounds of this group, their compositions, and the nature of the ions that they yield are again (as for compounds of the first group) closely dependent on the electrolytic dissocation of the interhalogen compounds themselves. Their Trouton constants (Table 2) and other data show that interhalogen compounds are associated in the liquid state and in some solvents. For their dimeric molecules the ionization process can be represented as follows:

$$(ICl)_2 \rightleftarrows I^+ + ICl_2^- \quad [28,9]$$
$$(BrF_3)_2 \rightleftarrows BrF_2^+ + BrF_4^- \quad [29, 30]$$
$$(IF_5)_2 \rightleftarrows IF_4^+ + IF_6^- \quad [30]$$

Hence, when interhalogen compounds react, in the melted condition or in solution, with halides of other elements, complex halides of two types may be formed: the interhalogen compounds may form a cation, or may enter into the composition of a complex anion. In fact, when the data in the literature and the results of the researches of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR on the compositions and structures of complex compounds formed by bromine and iodine halides with the halides of other elements are generalized, it is found that such complexes can be divided into "cationic" and "anionic". Examples of such complexes are given in Table 3.

TABLE 3

Cationic and Anionic Complexes formed by Bromine and Iodine Halide with Halides of other elements

Interhalogen compound	Cationic complexes	Anionic complexes
ICl	$I[AlCl_4] \cdot ICl$	$K[ICl_2]$
	$I[SbCl_6] \cdot nICl$; n = 1 and 2	$[PCl_4][ICl_2]$
	$I[SbCl_4 \cdot nICl$; n = 3 and 4	
IBr	$I[AlBr_4]$	$K[IBr_2]$
		$[PBr_4][IBr_2]$
BrF_3	$[BrF_2][SbF_6]$	$K[BrF_4]$
	$[BrF_2]_2[SnF_6]$	$Ba[BrF_4]_2$
	$[BrF_2][SO_3F]$	$Ag[BrF_4]$
ICl_3		$K[ICl_4]$
		$H[ICl_4] \cdot 4H_2O$
IF_5	$[IF_4][BF_4]$	$K[IF_6]$
	$[IF_4][SbF_6]$	

These complex compounds, both cationic and anionic, can be prepared by direct reaction with halides in melts or solutions. Some indirect methods are also known for the preparation of such complex compounds. These are based mainly on oxidation reactions, e.g. the action of iodine on PCl_5 or PBr_5, which proceeds as follows (X = Cl or Br):

$$PX_5 + I_2 \rightleftarrows PX_3 + 2IX$$

$$\frac{2PX_5 + 2IX = 2[PX_4][IX_2]}{3PX_5 + I_2 = 2[PX_4][IX_2] + PX_3} \quad [11,12,31]$$

Among the compounds given in Table 3 there are some double halides having an iodine cation, which were first prepared or investigated at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR (Fialkov [32], Kaganskaya [9], Shor [33], Abarbarchuk [34]*); and there are also some compounds having a tetrahalophosphonium cation, the structures of which were established by the author in collaboration with Kuzmenko [11, 12, 31]; these belong to a new class of complex compounds having a complex "acidocation" [37], in which the central atom is of a metalloid.

Complexes containing the difluorobromonium BrF_2^+ and tetrafluoroiodonium IF_4^+ cations belong to the same class of complex compounds. These double halides, and also compounds having the complex anions BrF_4^- and IF_6^-

* The only previously known compounds of this type were $SbCl_5 \cdot 2ICl$ and $SbCl_5 \cdot 3ICl$, which were discovered by Ruff and coworkers [35, 36]. There is no information about the nature of these compounds in Ruff's papers.

were prepared by Emeleus and his coworkers [30, 38].

Interhalogen compounds—in that they enter into the compositions of both cationic and anionic complexes, now forming the cation, and now the anion of double halides - have a dual function (a peculiar "amphotericity"••), for example:

$$ICl + C_5H_5N \rightarrow [C_5H_5N-I] + Cl^-;$$

$$ICl + PCl_5 \rightarrow [PCl_4]^+ + [ICl_2]^-;\ AlCl_3 + ICl \rightarrow I^+ + [AlCl_4]^-;$$

$$BrF_3 + KF \rightarrow K^+ + BrF_4^-;\ SbF_5 + BrF_3 \rightarrow BrF_2^+ + SbF_6^-.$$

The fact that PCl_5 and $SbCl_5$ form complexes of different types with iodine chloride - $[PCl_4][ICl_2]$ and $I[SbCl_6]$ (see Table 3) - is to be explained by their difference in structure and polarizability [42]. As is well known, PCl_5 and $SbCl_5$, in the form of separate molecules, both have the structure of a trigonal bipyramid, but whereas PCl_5 forms a crystalline lattice consisting of tetrahedral cation $[PCl_4]^+$ and octahedral anions $[PCl_6]^-$ and can react with various substances in the form $[PCl_4]Cl$, e.g. $[PCl_4]Cl + ICl = [PCl_4][ICl_2]$, such properties are not possessed by antimony pentachloride.

It is interesting also to note the differing behaviors of PCl_3, $AsCl_3$, and $SbCl_3$ toward iodine chloride. PCl_3 is readily oxidized by iodine chloride, forming first PCl_5, and the $[PCl_4]ICl_2$ [3]. $SbCl_3$ is not oxidized, but it combines with ICl. $AsCl_3$, however, as Abarbarchuk showed [43], does not react at all with iodine chloride; it is neither oxidized by it, nor does it combine with it. These facts are to be explained by the differences in the reducing properties of PCl_3, $SbCl_3$, and $AsCl_3$ and by the steric factor - the relations between the ionic radii.

The data that we have given confirm the great and varied scientific interest that the interhalogen compounds have for the chemistry of complex compounds. The practical application of the interhalogen compounds and the complex compounds that they form is based on their high reactivities and the variety of their chemical properties. Halogen fluorides are already being used for the fluorination of inorganic and organic compounds and for the preparation of the complex fluorides of various elements. The high activity of halogen fluorides as fluorinating agents, which is often equal to or greater than that of fluorine, is in some cases to be explained by the formation of more or less stable complex fluorides by the action of the halogen fluorides on inorganic substances. For example, complex fluorides of the type $M(RF_n)_m$ may be obtained by the action of BrF_3 on a mixture of a halide or oxyacid salt of the given cation and the stoichiometric amount of a halide or oxide of the element that is to form the central atom of the complex. In this way the preparation has been effected of, for example, hexafluoniobates, hexafluotantalates [44], fluopalladates, fluoplatinates [45], and similar complexes.

The fluorinating action of BrF_3 has been described in greatest detail [38]. BrF_3 is preferred for this purpose because the reaction can be carried out in the liquid phase at room temperature. The reaction is often quantitative. When reaction tends to be violent, it can be moderated by addition of dry bromine to the reaction mixture. Obstacles to the wide practical application of BrF_3 are its toxicity and its action in producing severe burns, similar to those caused by hydrogen fluoride.

As a second example of complex compounds of interhalogen compounds which are used in practice we must mention the complex acid $HICl_2$ and $HICl_4$, which are contained in hydrochloric acid solutions of ICl and ICl_3 respectively. Such solutions can be readily prepared by the action of hydrochloric acid on stoichiometric amounts of KI (or iodine) and KIO_3. When there is a certain excess of hydrochloric acid, these solutions are very stable. In hydrochloric acid solution these complex acids are in equilibrium with their dissociation products, which include I^+ ions.

Gengrinovich, who carried out the first investigations in this field, Shakh, Kagan [46-51], and others, working in the author's laboratory and in other institutes, have developed numerous methods for the quantitative volumetric determination of inorganic and organic substances based on oxidation, replacement, double-bond addition, and complex-forming reactions of iodine derivatives of organic substances, and also on methods for the preparation of these substances. The reactions proceed quantitatively, and very pure products are obtained, contamination with chlorine-substituted products being negligible.

There is every reason to suppose that interhalogen compounds and the complex compounds derived from them will find a much wider application in practice. It is therefore necessary to intensify investigation on the chemistry of the complex compounds of interhalogen compounds both preparative and physicochemical.

•• This peculiarity of interhalogen compounds brings the investigations in this field close to the problem of acid-base interaction [39, 40, 41].

SUMMARY

1. Investigations on interhalogen compounds and the complex compounds that they form have made it possible to establish the structures of many such complex compounds, their chemical properties, and the nature of the ions that they form.

2. Double halides have been prepared in which iodine is present as a cation.

3. The field of complex compounds in which the central atom is a nonmetal has been extended.

4. It has been shown that complex compounds containing "acidocations" having a metalloid as central atom, are found more frequently than was previously thought.

5. Some generalizations have been made regarding the relation between the chemical properties and structures of complex compounds and the structures and polarizabilities of the original interhalogen molecules.

6. Some new ways have been found for the practical application of iodine halides (ICl and ICl_3), for the quantitative determination of inorganic and organic substances, and for the preparation of iodine derivatives.

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Received July 4, 1954

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* See Consultants Bureau English translation. page 1191, a-235.

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ACTION OF SULFURIC ACID ON 2-METHYLTHIOPHENE

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As an examination of the literature will show, the sulfonation of thiophene has been studied fairly thoroughly. When thiophene is treated in the cold with concentrated sulfuric acid in presence of a large amount of an indifferent solvent, the main product is 2-thiophenesulfonic acid, and a small amount of 2,2'-bithiophene is obtained as by-product [1]. The sulfonation of thiophene homologs under the same conditions proceeds more vigorously and is accompanied by much resinification, and the resulting mixture of sulfonic acids and products arising by polymerization, condensation, and oxidation is difficult to separate [2].

Sulfonic acids of thiophene homologs have generally been prepared by double decomposition between acetyl derivatives of the parent compounds and concentrated sulfuric acid. Recently, pyridine-sulfur trioxide and dioxan - sulfur trioxide have been successfully applied for the sulfonation of thiophene and other acidophobic heterocyclic compounds [3]. Although the direct sulfonation of thiophene homologs has lost much of its importance since the development of improved methods of preparing sulfonic acids, the study of processes occurring when sulfuric acid reacts with thiophene homologs is of more than theoretical interest. Thus, this process lies at the basis of the manufacture of ichthyol, a medicinal prepared by the sulfonation of shale tar distillates rich in thiophene derivatives.

In our work on the improvement of the quality of ichthyol [4] and the preparation of the medicinal albichthyol, which can replace ichthyol and is more effective [5], it became necessary to study the side reactions accompanying sulfonation of thiophene derivatives. In view, however, of the great difficulties presented by the isolation of individual substances from the mixtures obtained by the sulfonation of shale tar distillates, we decided to investigate the sulfonation of individual thiophene derivatives - in the first place 2-methylthiophene, prepared synthetically. In the present investigation we have studied the following factors: amount and concentration of sulfuric acid, temperature, and duration of reaction.

The reaction was carried out in presence of petroleum ether (5:100). When 2-methylthiophene was sulfonated under conditions close to those used in the manufacture of ichthyol (slightly fuming sulfuric acid containing about 0.5% of free sulfur trioxide; temperature 55-50°; duration of reaction 30 minutes), there was copious evolution of sulfur dioxide, and much resinification occurred.

No individual substance could be isolated from the resin. When the temperature was lowered to 25-30° and the duration of the reaction was reduced to 2.5-3 hours, a new sulfonic acid was isolated from the sulfonation products. This substance differed greatly from the known sulfo derivatives of 2-methylthiophene, its salts, even the alkali-metal salts, having very low solubilities. The highest yield of this sulfonic acid was obtained when monohydrate was used, and a small change in the acid concentration in one direction or the other resulted in a reduction of yield (see the table). The crude sulfonic acid was obtained as a reddish-brown sirupy liquid. It was not found possible to isolate the free sulfonic acid in the pure state; it was highly soluble in water like the mono- and di-sulfonic acids of 2-methylthiophene, did not crystallize out from acid solutions, and could not be prepared by double decomposition of its lead salt with hydrogen sulfide, since its lead salt, unlike those of the known sulfonic acids of 2-methylthiophene, was completely insoluble in water.

The new sulfonic acid gave potassium, sodium, ammonium, and p-toluidine salts of low solubility at ordinary temperature, and its barium and lead salts were almost insoluble even at high temperatures. The elementary composition of the sulfonic acid was established by the elementary analysis of its ammonium and sodium salts and by analysis of the barium salt for barium and the p-toluidine salt for nitrogen. The molecular weight of the last salt was determined by the Rast method. The results of these determinations showed that the new sulfonic acid contained one sulfo group in its molecule and had a molecular formula of $C_{15}H_{14}S_4O_3$. We did not succeed in characterizing the sulfonic acid by means of its acid chloride or amide.

As a result of numerous experiments it was shown that reaction between the sodium salt of the sulfonic acid and phosphorus pentachloride proceeds readily in presence of absolute benzene at 40-45°, and that the product is soluble in benzene, but it was found impossible to isolate the substance from benzene because of its instability; as soon as benzene was removed, it resinified. Attempts to prepare the amide from the benzene solution

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* Deceased

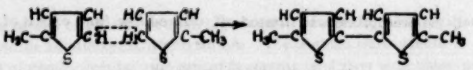
TABLE

No.1	Amount of		H_2SO_4 (g)	Density or concentration	Reaction temperature (°C)	Amount of ammonium salt (g)	Yield of ammonium salt (%)
	2-methylthiophene (g)	petroleum ether (ml)					
1	5	100	100	1.849 (20°)	25-30	0.1	1.5
2	5	100	100	1.840 (20°)	25-30	0.7	10.6
3	4.5	100	90	1.839 (20°)	25-30	1.2	20.2
4	10	200	200	1.838 (20°)	25-30	4.75	36.0
5	7	150	150	1.838 (20.5°)	25-30	2.5	27.3
6	10	200	200	1.837 (30°)	25-30	2.6	19.7
7	4	80	80	99.51%	20-30	1	18.9
8	9	300	180	99.36%	20-30	0.9	7.6

Note. H_2SO_4 of density 1.838 (20°) has a concentration of 100% (monohydrate).

of the sulfonyl chloride were also unsuccessful. Treatment of the sulfonyl chloride with ammonia resulted in the formation of a light-yellow waxy substance, which could not be purified because it was insoluble in all of the usual solvents. The melting point of this substance could not be determined, for, on being heated in a capillary, it sintered together and darkened in color.

Apart from the new sulfonic acid, a small amount of a solid substance was isolated from the unsulfonated resinous products. This substance, which crystallized from alcohol in the form of white plates melting at 63-66°, was of a neutral character and gave a positive reaction for sulfur and a not-altogether characteristic reaction for thiophenes with isatin and sulfuric acid. It was close in physical properties to 5,5'-dimethyl-2,2'-bithiophene, which was obtained synthetically by Steinkopf [6]. It is possible that this compound was formed by the oxidation of 2-methylthiophene by sulfuric acid, the reaction being analogous to that occurring in the sulfonation of thiophene and its chloro, bromo, and other derivatives:



In the sulfonation of 2-methylthiophene, apart from the above-described new sulfonic acid, other sulfonic acids were isolated in the form of their salts, which were readily soluble in water. Elementary analysis showed that they were mixtures of salts of mono- and di-sulfonic acids of 2-methylthiophene.

On the basis of our study of the composition of the new sulfonic acid we may make the following suggestions. The experimental conditions were favorable for reaction in the following three directions simultaneously: 1) sulfonation of 2-methylthiophene; 2) oxidative condensation with formation of bithiophenes and dithienylthiophenes; 3) sulfonation of the products of oxidative condensation. The structural formula of the new sulfonic acid may be represented tentatively: $C_4H_2CH_3S-C_4HCH_3S-C_4HCH_3S-SO_3H$.

EXPERIMENTAL

1. Sulfonation of 2-Methylthiophene

A solution of 10 g of 2-methylthiophene in 200 ml of petroleum ether was placed in a flask fitted with stirrer, thermometer, dropping funnel, and reflux condenser. The solution was stirred mechanically, and 200 g of sulfuric acid, sp. gr. $1.838^{20°}$ (monohydrate), was added from the dropping funnel at such a rate that the temperature of the reaction mixture did not exceed 30°. When the whole of the acid had been added, the mixture was stirred for three hours, the temperature being maintained at 25-30°.

At the end of the reaction the mixture was poured carefully into 200 ml of ice water cooled from without with a mixture of ice and salt; petroleum ether separated (this should not give a reaction for 2-methylthiophene). The aqueous solution was shaken in a separating funnel with 100 ml of ether and the mixture was allowed to settle. Three layers were formed: a) the top layer - an ether extract containing a small amount of sulfonic acids and resinous substances; b) the middle layer - a dark-colored sirupy liquid containing a mixture of sulfonic acids and also some aqueous sulfuric acid; c) the lower layer - a solution of sulfuric acid containing a small amount of sulfonic acids and resins.

The middle layer (about 20 ml), which contained products of the sulfonation of 2-methylthiophene, was dissolved in an equal volume of water and the solution was neutralized with 10% aqueous ammonia. During this last process the color of the solution changed first from brown to green and then, at the neutralization point, to yellow. A finely crystalline precipitate of a difficultly soluble ammonium salt separated. The mixture was set aside for some hours to allow the precipitation to proceed to completion. The product was 3.85 g of dry salt, which was of a yellowish color. A further 0.9 g of the salt was isolated from the ether extracts. The total yield was 4.75 g, i.e. 36.9% calculated as $C_{15}H_{13}S_3-SO_3NH_4$.

The mother liquid contained a mixture of readily soluble ammonium salts of mono- and di-sulfonic acids of 2-methylthiophene. The ammonium salt of the sulfonic acid investigated was recrystallized three times from hot water. The pure salt crystallized in the form of fine white scales having a silvery reflex. It was readily soluble in alcohol, but insoluble in ether and in benzene.

Found %:	N 3.52; 3.48;	S 33.39; 33.14;	C 45.87; H 4.80
$C_{15}H_{13}S_3-SO_3NH_4$. Calculated %:	N 3.61;	S 33.10;	C 46.46; H 4.39

2. Preparation of the Sodium Salt and Investigation of its Composition

The mixture of sulfonic acids prepared by sulfonation of 10 g of 2-methylthiophene under the above-described

conditions was dissolved in 20 ml of water, and the solution was neutralized with a 20% solution of sodium carbonate. A white precipitate of the difficultly soluble sodium salt separated. The mixture was set aside for some hours to allow precipitation to go to completion. The yield of the salt was 5.65 g, i.e. 42.3% calculated as

	Found %:	Na 5.70; 5.81; S 32.36; 32.53
$C_{15}H_{13}S_3-SO_3Na$.	Calculated %:	Na 5.86; S 32.68

3. Preparation of the Barium Salt

The recrystallized ammonium salt (1 g) was dissolved in 400 ml of distilled water, and the solution was heated to boil. Two or three drops of concentrated sulfuric acid were added, and then 4 ml of a 10% solution of barium chloride. A voluminous white precipitate formed.

When the mixture was cool, the precipitate was filtered off, washed free from excess of barium ions and dried to constant weight.

	Found %:	Ba 15.40; 15.46
$C_{15}H_{13}S_3-SO_3\frac{Ba}{2}$	Calculated %:	Ba 15.67;

4. Preparation of the p-Toluidine Salt and Determination of its Molecular Weight

A solution of 0.4 g of p-toluidine in acetic acid was added to a solution of 1 g of the ammonium salt $C_{15}H_{13}S_3-SO_3NH_4$ in 100 ml of water heated to 50-60°. When the solution was cooled, a voluminous white precipitate of the p-toluidine salt formed. The salt dissolved when warmed with water, alcohol, or benzene. It was recrystallized from water and then melted at 170-171°.

	Found %:	N 3.11
$C_{15}H_{13}S_3-SO_3NH_3C_6H_4CH_3$.	Calculated %:	N 2.93
	Found M:	455.82; 471.15 (Rast's method)
$C_{15}H_{13}S_3-SO_3NH_3C_6H_4CH_3$.	Calculated M:	477.43

SUMMARY

1. When 2-methylthiophene is reated with sulfuric acid of specific gravity $1.838^{20°}$ (monohydrate) at 25-30° in presence of an indifferent solvent (petroleum ether), a new sulfonic acid - a methyl[methyl(methylthienyl)thienyl] thiophenesulfonic acid - is obtained in a yield of 36% (isolated as ammonium salt) or 46% (isolated as sodium salt).

2. The ammonium, sodium, barium, and p-toluidine salts of this sulfonic acid have been prepared and characterized.

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Received February 15, 1954.

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REACTION OF ALKYL ORTHOTITANATES WITH TITANIUM TETRACHLORIDE IN A PIPERIDINE MEDIUM

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The reaction between alkyl orthotitanates and titanium tetrachloride (the reverse of disproportionation) is of interest for the synthesis of alkoxychlorotitaniums of general formula $(RO)_nTiCl_{4-n}$ (n = 1, 2, or 3), because alkyl orthotitanates are now fairly readily accessible. In the conversion of an alkyl orthotitanate into alkoxychlorotitaniums in this way, the total number of Ti—OAlk linkages in the products is the same as the number in the original alkyl orthotitanate.

According to the results of British chemists [1], reaction of an alkyl orthotitanate with a large excess of titanium tetrachloride yields an alkoxytrichlorotitanium. The authors were unable to isolate pure dialkoxydichlorotitaniums by the use of equimolecular amounts of reactants, and they concluded that mixtures of products containing different numbers of alkoxyl groups in their molecules were formed under these conditions. The authors did not attempt to obtain trialkoxychlorotitaniums by this method; their general conclusion was that the reaction between alkyl orthotitanates and $TiCl_4$ could be used only for the preparation of alkoxytrichlorotitaniums, for which purpose an excess of $TiCl_4$ was required.

In a previous paper [2] we stated that, by carrying out the reaction between alkyl orthotitanates and $TiCl_4$ taken in proportions corresponding precisely to the equations (I), (II), and (III) in a medium of benzene and petroleum ether at room temperature, we had obtained trialkoxychloro-, dialkoxydichloro-, and alkoxytrichlorotitaniums in high yields.

$$3(RO)_4Ti + TiCl_4 = 4(RO)_3TiCl; \quad (I)$$

$$(RO)_4Ti + TiCl_4 = 2(RO)_2TiCl_2; \quad (II)$$

$$(RO)_4Ti + 3TiCl_4 = 4ROTiCl_3 \quad (III)$$

It was found that dialkoxydichloro- and alkoxytrichloro-titaniums sometimes decomposed (underwent disproportionation) during vacuum distillation, so that it was better to purify these substances by recrystallization from benzene or from a mixture of benzene and petroleum ether.

We found that alkyl orthotitanates and trialkoxychloro-, dialkoxydichloro-, and alkoxytrichloro-titaniums formed crystalline double compounds with piperidine of composition $(RO)_nTiCl_{4-n}C_5H_{10}NH$, (n = 1, 2, 3, or 4). When the double compound of ethyl orthotitanate and piperidine was recrystallized and dried, it lost part of its piperidine, but the double compounds formed with alkoxychlorotitaniums withstood repeated recrystallization. All of the double compounds were extremely hygroscopic. When heated in a sealed capillary, they melted over a wide range of temperature. It should be noted that the structures of these compounds are difficult to understand from the point of view of coordination theory, which would lead us to expect the formation of compounds in which the coordination number of the titanium would be six.

We have made use of the ability of alkoxychlorotitaniums to give stable double compounds with piperidine in order to isolate them in the form of these compounds from the reaction mixtures obtained by treating alkyl orthotitanates with $TiCl_4$. The alkyl orthotitanate, titanium tetrachloride, and piperidine were taken in the proportions required by equations (IV), (V), and (VI), and the double compounds formed by piperidine with trialkoxychloro-, dialkoxydichloro-, and alkoxytrichloro-titanium, respectively, were obtained:

$$3(RO)_4Ti + TiCl_4 + 4C_5H_{11}N = 4(RO)_3TiCl \cdot C_5H_{11}N. \quad (IV)$$

$$(RO)_4Ti + TiCl_4 + 2C_5H_{11}N = 2(RO)_2TiCl_2 \cdot C_5H_{11}N. \quad (V)$$

$$(RO)_4Ti + 3TiCl_4 + 4C_5H_{11}N = 4ROTiCl_3 \cdot C_5H_{11}N. \quad (VI)$$

We have shown also that reaction between chlorotriethoxytitanium, $TiCl_4$, and piperidine taken in the proportions required by equation (VII) results in the formation of the double compound of piperidine and dichlorodiethoxytitanium:

$$2(RO)_3TiCl + TiCl_4 + 3C_5H_{11}N \rightarrow 3(RO)_2TiCl_2 \cdot C_5H_{11}N. \quad (VII)$$

These experiments have shown, first the wide applicability of this reaction of disproportionation in reverse, and second that when carried out in a piperidine medium the reaction goes smoothly and gives a good yield of

the double compounds.

When the double compound $(C_2H_5O)_3TiClC_5H_{10}NH$ was treated with ethyl alcohol, a smooth reaction occurred with formation of ethyl orthotitanate and piperidine hydrochloride. In the same way, when the double compounds $(n\text{-}C_3H_7O)_2TiCl_2 \cdot C_5H_{10}NH$ and $(n\text{-}C_4H_9O)_2TiCl_2 \cdot C_5H_{10}NH$ were treated with propyl alcohol and butyl alcohol respectively, chlorotripropoxy- and tributoxychloro-titaniums were formed according to the equations:

$$(n\text{-}C_3H_7O)_2TiCl_2 \cdot C_5H_{10}NH + n\text{-}C_3H_7OH \rightarrow (n\text{-}C_3H_7O)_3TiCl + C_5H_{11}N \cdot HCl.$$

$$(n\text{-}C_4H_9O)_2TiCl_2 \cdot C_5H_{10}NH + n\text{-}C_4H_9OH \rightarrow (n\text{-}C_4H_9O)_3TiCl + C_5H_{11}N \cdot HCl.$$

EXPERIMENTAL

1. Preparation of $(C_2H_5O)_3TiCl \cdot C_5H_{10}NH$

A. From Chlorotriethoxytitanium and Piperidine. Piperidine (2.57 g, i.e. 0.030 mole) was added, with cooling, to 5.30 g (0.024 mole) of chlorotriethoxytitanium, and the mixture solidified. The resulting compound was recrystallized from a mixture of two parts of benzene and one part of petroleum ether. The double compound is readily soluble in chloroform and benzene, but not so readily soluble in petroleum ether.

Found %: C 43.60; 43.28; H 8.77; 8.58; Ti 15.84; 15.85; N 4.61; 4.58

$(C_2H_5O)_3TiClC_5H_{10}NH$. Calculated %: C 43.49; H 8.63; Ti 15.78; N 4.61

B. From Ethyl Orthotitanate. A solution of 3.40 g (0.040 mole) of piperidine in 5 ml of benzene was added, with cooling, to 6.84 g (0.030 mole) of ethyl orthotitanate in 15 ml of benzene, and then a solution of 1.89 g (0.010 mole) of $TiCl_4$ in 4 ml of benzene was added dropwise. The double compound crystallized out from the solution. In order to effect more complete precipitation, 20 ml of petroleum ether (b.p. 50-70°) was added to the mixture. The yield of product was 6.6 g (54%); it was recrystallized from a mixture of benzene and petroleum ether.

Found %: C 43.07; 43.27; H 8.82; 8.88; Ti 16.04; 16.18; N 4.55; 4.63

2. Preparation of $(n\text{-}C_3H_7O)_3TiCl \cdot C_5H_{11}N$ from Chlorotripropoxytitanium

Piperidine (2 ml) was added, with cooling, to a solution of 2.2 g of chlorotripropoxytitanium in 1 ml of petroleum ether. The double compound crystallized out, and it was filtered off and recrystallized from benzene.

Found %: C 48.53; 48.51; H 9.31; 9.12; N 4.22; 4.05

$(n\text{-}C_3H_7O)_3TiClC_5H_{11}N$. Calculated %: C 48.61; H 9.33; N 4.05

3. Preparation of $(n\text{-}C_3H_7O)_2TiCl_2 \cdot C_5H_{10}NH$ from Propyl Orthotitanate

To a cooled solution of 2.84 g (0.010 mole) of propyl orthotitanate in 3 ml of benzene, first of all a solution of 1.72 g (0.020 mole) of piperidine in 2 ml of benzene was added, and then a solution of 1.9 g (0.010 mole) of $TiCl_4$ in 4 ml of benzene; the solution became dark in color. The reaction mixture was heated at 60° for ten minutes, and then cooled. Petroleum ether (8 ml) was added, and the precipitate that formed was filtered off. The yield was 5 g (78%). A completely colorless product was obtained when the precipitate was recrystallized from a mixture of equal volumes of benzene and petroleum ether.

Found %: C 41.25; 41.49; H 7.94; 8.09; N 4.42; 4.51;

$(C_3H_7O)_2TiCl_2C_5H_{11}N$. Calculated %: C 40.99; H 7.82; N 4.34

4. Preparation of $(C_2H_5O)_2TiCl_2 \cdot C_5H_{10}NH$ from Chlorotriethoxytitanium

To a cooled solution of 2.06 g (0.0094 mole) of chlorotriethoxytitanium in 5 ml of benzene, first of all a solution of 1.19 g (0.0139 mole) of piperidine in 4 ml of benzene was added, and then a solution of 0.90 g (0.0047 mole) of $TiCl_4$ in 4 ml of benzene. The reaction mixture was heated for 30 minutes at 60-65°. The yield of crystalline product, which separated when the mixture was cooled, was 3.3 g (79%). The double compound was recrystallized from a mixture of benzene and chloroform.

Found %: C 36.79; 36.84; H 7.55; 7.42; N 4.57; 4.69

$(C_2H_5O)_2TiCl_2C_5H_{10}NH$. Calculated %: C 36.74; H 7.19; N 4.76

5. Preparation of $(n\text{-}C_4H_9O)_2TiCl_2 \cdot C_5H_{11}N$

A. From Butyl Orthotitanate. To a cooled solution of 3.4 g (0.010 mole) of butyl orthotitanate in 3 ml of benzene, first of all a solution of 1.7 g (0.020 mole) of piperidine in 1 ml of benzene was added, and then a solution of 1.9 g (0.010 mole) of $TiCl_4$ in 3 ml of benzene. The reaction mixture, which had become dark in color, was heated for ten minutes at 50-60°. The mixture was diluted with 10 ml of petroleum ether and then cooled well, and a crystalline precipitate was obtained; the yield was 5 g (85%). The double compound was recrystallized from a mixture of benzene and petroleum ether.

	Found %:	Ti 13.63; 13.70; N 4.05; 4.02
$(C_4H_9O)_2TiCl_2C_5H_{10}NH$.	Calculated %:	Ti 13.68; N 4.00

B. From Tributoxychlorotitanium. The procedure followed that of Expt. No. 4, and 2.7 g of tributoxychlorotitanium, 1.13 g of piperidine, and 0.84 g of $TiCl_4$ in a benzene medium yielded 2 g (57%) of the double salt of piperidine and dibutoxydichlorotitanium. For anaylsis the product was recrystallized from a mixture of petroleum ether and benzene.

	Found %:	C 44.78; 44.60; 44.47; H 8.55; 8.39; 8.60; N 4.05; 4.03
$(C_4H_9O)_2TiCl_2C_5H_{11}N$.	Calculated %:	C 44.57; H 8.35 N 4.00

6. Preparation of $n\text{-}C_3H_7OTiCl_3C_5H_{10}NH$ from Propyl Orthotitanate

To a solution of 1.42 g (0.005 mole) of propyl orthotitanate in 20 ml of a mixture of equal volumes of benzene and petroleum ether, first of all a solution of 1.70 g (0.020 mole) of piperidine in 4 ml of benzene was added, and then a solution of 2.84 g (0.015 mole) of $TiCl_4$ in 4 ml of benzene. The reaction mixture turned orange at first, and later became greenish tellow. Petroleum ether (15 ml) was added, and 5.2 g (87%) of precipitate was separated. The product was recrystallized from benzene.

	Found %:	C 32.18; 32.46; H 6.17; 6.23; Ti 15.79; 15.68; N 4.65; 4.71
$C_3H_7OTiCl_3C_5H_{10}NH$.	Calculated %:	C 32.16; H 6.07; Ti 16.06; N 4.69

7. Preparation of $n\text{-}C_4H_9OTiCl_3C_5H_{10}NH$ from Butyl Orthotitanate

The procedure followed that of the preceding experiment, and 1.70 g of butyl orthotitanate, 1.70 g of piperidine, and 2.84 g of $TiCl_4$ yielded 5 g (80%) of the double compound, which was recrystallized from benzene.

	Found %:	C 35.11; 34.98; H 6.48; 6.51; N 4.46; 4.25; Cl 34.19; 34.25
$C_4H_9OTiCl_3C_5H_{11}N$.	Calculated %:	C 34.58; H 6.44; N 4.48; Cl 34.07

8. Preparation of $CH_2{=}CH-CH_2OTiCl_3C_5H_{10}NH$

The procedure was that of the preceding experiments, and 1.44 g of allyl orthotitanate, 1.73 g of piperidine, and 2.90 g of $TiCl_4$ yielded 4.8 g (77%) of the double compound, which was recrystallized from benzene.

	Found %:	C 32.73; 32.79; H 5.60; 5.62
$CH_2{=}CHCH_2OTiCl_3 \cdot C_5H_{10}NH$.	Calculated %:	C 32.40; H 5.43;

9. Action of Ethyl Alcohol on $(C_2H_5O)_3TiClC_5H_{11}N$

The recrystallized double compound $(C_2H_5O)_3TiClC_5H_{11}N$ (9.5 g) was dissolved in 30 ml of benzene, and to the clear filtered solution 1.4 g of absolute ethyl alcohol was added at room temperature. There was an immediate precipitate of piperidine hydrochloride. The reaction mixture was cooled, and the precipitate was separated, washed with petroleum ether, and dried over $CaCl_2$. The yield of product was 1.3 g (83%); after recrystallization from alcohol it melted at 244-245°. Solvent was driven from the filtrate at the water pump (80°, 40 mm). The residue weighed 5.3 g (74%). The ethyl orthotitanate obtained distilled over at 127-127.5° at 1.5 mm, and had n_D^{20} 1.5105. For ethyl orthotitanate the literature [3] gives b.p. 128-129° (1.5 mm).

10. Action of Propyl Alcohol on $(n\text{-}C_3H_7O)_2TiCl_2C_5H_{11}N$

The prodecure of the preceding experiment was followed, and 8.6 g of the double compound $(n\text{-}C_3H_7O)_2TiCl_2C_5H_{11}N$ and 3 ml of absolute propyl alcohol in a benzene medium yielded 4.5 g (65%) of chlorotripropoxytitanium and 3.2 g (93%) of piperidine hydrochloride. The resulting chlorotripropoxytitanium distilled over at 148-149° (5 mm) and was analyzed in the form of its double salt with piperidine (for analytical results see Expt. No. 2).

11. Action of Butyl Alcohol on $(n\text{-}C_4H_9O)_2TiCl_2 \cdot C_5H_{11}N$

The procedure was that of the last two experiments, and 10.7 g of the double compound $(n\text{-}C_4H_9O)_2TiCl_2C_5H_{11}N$ and 5 ml of absolute butyl alcohol in a benzene medium yielded 7.3 g (79%) of crude tributoxychlorotitanium and 3.4 g (91%) of piperidine hydrochloride. The resulting tributoxychlorotitanium distilled over at 165-166° (4 mm). It was converted into the double compound of dibutoxydichlorotitanium, and piperidine which was analyzed (for analytical results see Expt. No. 5B).

SUMMARY

1. It has been shown that alkyl orthotitanates and trialkoxychloro-, dialkoxydichloro-, alkoxytrichloro-titaniums form crystalline double compounds with piperidine having the composition $(RO)_nTiCl_{4-n} \cdot C_5H_{10}NH$, n = 1, 2, or 3).

2. It has been found that the reaction between alkyl orthotitanates and titanium tetrachloride (the reverse of disproportionation) proceeds smoothyl in presence of the calculated amount of piperidine with formation of double compounds of piperidine with alkoxychlorotitaniums in high yield.

3. Double compounds of the following compositions have been prepared:

$(C_2H_5O)_3TiCl \cdot C_5H_{10}NH$; $(n\text{-}C_3H_7O)_3TiCl \cdot C_5H_{10}NH$;

$(C_2H_5O)_2TiCl_2 \cdot C_5H_{10}NH$; $(n\text{-}C_3H_7O)_2TiCl_2 \cdot C_5H_{10}NH$;

$(n\text{-}C_4H_9O_2TiCl_2 \cdot C_5H_{10}NH$; $n\text{-}C_3H_7OTiCl_3 \cdot C_5H_{10}NH$;

$n\text{-}C_4H_9OTiCl_3 \cdot C_5H_{10}NH$; $CH_2=CH-CH_2OTiCl_3 \cdot C_5H_{10}NH$

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Received January 19, 1954

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SYNTHESIS OF STEREOISOMERIC ORGANOMERCURY COMPOUNDS VIA ORGANOLITHIUM COMPOUNDS

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In a series of investigations carried out in our laboratory a study has been made of the stereochemistry of metal-exchange reactions given by cis-and trans-2-chlorovinyl organometallic compounds [1-6]. In a paper by two of the present authors it was concluded that in electrophilic and radical exchange reactionsof metal attached to an olefin carbon the geometric configuration is retained [7].

It was important to verify the correctness of this conclusion by examining the behavior of organometallic compounds in which an unsaturated purely hydrocarbon radical is attached to metal at the olefin carbon responsible for the geometric isomerism.

Very few such compounds are described in the literature; those described are mainly organomagnesium and organolithium compounds that have not been isolated in the pure state (8-12). Practically nothing is known about alkenyl derivatives of heavy metals [13]. Styrylmercury, styryltin, and styrylthallium derivatives have been prepared by one of us, working with Kudryavtseva, but each of them was obtained in only one stereoisomeric form [14]. Hence, in order to carry out the desired investigation it was first necessary to synthesize the cis and trans forms of suitable mercury derivatives of hydrocarbons in which the metal was attached to an unsaturated carbon. The present paper deals with the synthesis of stilbene derivatives of this type. We prepared them by double decomposition between the geometric isomers of 1,2-diphenylvinyllithium [12] and mercuric chloride:

$$C_6H_5CH=CBrC_6H_5 \xrightarrow{C_4H_9Li} C_6H_5CH=CLiC_6H_5 \xrightarrow{HgCl_2} [C_6H_5CH=CC_6H_5]_2\,Hg.$$

1,2-Diphenylvinyllithium was formed when trans-α-bromostilbene was treated with butyllithium in an ether-benzene medium at a temperature of −30° to −20°. When mercuric chloride was added slowly at the same temperature to the resulting solution of the lithium reagent, a precipitate of bis(1,2-diphenylvinyl)mercury began to form. This compound was found to be of very low solubility in benzene, and practically insoluble in ether, alcohol, chloroform, and acetone. It could be recrystallized from xylene and dioxan and it melted at 243-244°, without decomposition. Yields of 50-60% of bis(1,2-diphenylvinyl)mercury were attained. From the ether-benzene solution obtained after decomposition of the reaction mixture and separation of the insoluble bis(1,2-diphenylvinyl)mercury, it was possible to isolate a very small amount of 1,2-diphenylvinylmercury chloride, and also unchanged trans-α-bromostilbene (30-40% of the amount taken for reaction).

It was shown that raising the reaction temperature lowered the yield of the mercury compound, and that increase in the duration of the reaction had no effect on the yield. In all of the experiments the main product was bas(1,2-diphenylvinyl)mercury, and 1,2-diphenylvinylmercury was obtained as a by-product, irrespective of the molar proportions of reactants and the order of their addition.

1,2-Diphenylvinyllithium was also prepared directly by reaction of trans- α-bromostilbene with lithium in ether at 20-35°. When treated with mercuric chloride, the resulting lithium reagent yielded bis(1,2-diphenylvinyl) mercury (m.p. 243-244°) in 29% yield and 1,2-diphenylvinylmercury chloride in 13% yield.

After being heated for a long time with an alcoholic solution of mercuric chloride, the high-melting bis (1,2-diphenylvinyl)mercury reacted with formation of 1,2-diphenylvinylmercury chloride in almost quantitative yield. This compound melted at 141-142°; it was found to be highly soluble in alcohol and chloroform, and moderately soluble in benzene. It was symmetrized when treated with potassium iodide in acetone solution, yielding the original bis(1,2-diphenylvinyl)mercury, m.p. 243-244°.

It was symmetrized also when treated with butyllithium. In this reaction no formation of mercury was observed, and it is possible that symmetrization by means of butyllithium passes through the stage of an unstable unsymmetrical full organomercury compound:

$$2C_6H_5CH=C(HgCl)C_6H_5 + 2C_4H_9Li \rightarrow [2C_6H_5CH=C(HgC_4H_9)C_6H_5 + 2LiCl] \rightarrow$$

$$\rightarrow [C_6H_5CH=CC_6H_5]_2\,Hg + (C_4H_9)_2Hg.$$

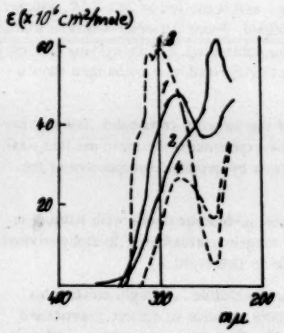
The synthesis of the other stereoisomer of the stilbene mercury derivative was effected by a procedure analo-

ous to that described for the compound of m.p. 243-244°. For this isomer, however, some difficulties were encountered, and it was found that only by the observation of strictly defined conditions during the preparation of the lithium reagent could an organomercury compound stereoisomeric to the above-described bis(1,2-diphenylvinyl) mercury be obtained. Thus, when the reaction between cis-α-bromostilbene and butyllithium was carried out at a temperature not exceeding −40° to −35° and in as short a time as possible, a 50% yield was obtained of a bis(1,2-diphenylvinyl)mercury of m.p. 145-147°, very soluble in benzene and moderately soluble in chloroform and alcohol. If, however, the temperature was raised or the duration of reaction was increased in the reaction between cis-α-bromostilbene and butyllithium, then in the subsequent reaction with mercuric chloride, the bis(1,2-diphenylvinyl)mercury of m.p. 243-244° given by trans-α-bromostilbene was formed as by-product, or even as the main product.

When the bis(1,2-diphenylvinyl)mercury of m.p. 145-147° reacted with an alcoholic solution of mercuric chloride, the product was a 1,2-diphenylvinylmercury chloride of m.p. 130-131°, stereoisomeric with the above-described compound of m.p. 141-142°. The substance of m.p. 130-131° was found to be more soluble in methanol, ethanol, and chloroform than the substance of m.p. 141-142°.

When treated with potassium iodide or butyllithium, the low-melting stereoisomer of 1,2-diphenylvinylmercury chloride was symmetrized, yielding the low-melting bis(1,2-diphenylbinyl)mercury. We thus have four organomercury compounds: the stereoisomeric 1,2-diphenylvinylmercury chlorides, melting at 141-142° and 130-131°, and the stereoisomeric bis(1,2-diphenylvinyl)mercurys, melting at 243-244° and 145-147°.

We have tentatively ascribed the trans configuration to the higher-melting member of each pair, and the cis configuration to the lower-melting member. We based our choice on the following considerations: 1) usually, though not always, the stereoisomer having the higher melting point and lower solubility has the trans configuration, and the lower-melting, more readily soluble isomer has the cis configuration; 2) when heated, the lower-melting bis(1,2-diphenylvinyl)mercury is converted into the higher-melting stereoisomer, and it is known that the thermal isomerization of other substances of similar structure is generally in the direction of cis to trans, cis-α-bromostilbene being converted into the trans isomer [15] and cis-stilbene into trans-stilbene [16] (the low-melting bis(1,2-diphenylvinyl) mercury is isomerized also by ultraviolet radiation, a fact that does not conflict with the assumed configuration, since, although trans-cis isomerizations often occur in ultraviolet radiation, cis-trans conversions are also known); 3) confirmation of the assumed configurations was found in observations made* of the ultraviolet absorption spectra of stereoisomeric 1,2-diphenylvinylmercury chlorides (see figure).



Ultraviolet absorption spectra: 1) 1,2-diphenylvinylmercury chloride of m.p. 141-142°; 2) 1,2-diphenylvinylmercury chloride of m.p. 130-131° ($c = 0.38 \cdot 10^{-4}$ mole per liter of CH_3OH); 3) trans-stilbene; 4) cis-stilbene [18].

Definite geometric configurations have often been ascribed to substances on the basis of differences in the ultraviolet spectra of isomers. There is an empirical rule to the effect that trans isomers absorb more strongly in the ultraviolet than cis isomers [17]. The ultraviolet spectra of the stereoisomeric stilbenes [18, 19] and some of their derivatives [20, 21, 22] have been described in the literature; they are in accord with the above rule. It will be seen from the curves given that 1,2-diphenylvinylmercury chloride of m.p. 141-142° absorbs almost twice as strongly as the isomer of m.p. 130-131° (the first absorption maxima on the curves 1 and 2 in the region of 283-275 mμ).

Moreover, when the substances of m.p. 141-142° and 243-244° obtained from trans-α-bromostilbene are decomposed with dilute hydrochloric acid, trans-stilbene is formed quantitatively, and when the substances of m.p. 130-131° and 145-147° obtained from cis-α-bromostilbene are decomposed under the same conditions, the product is cis-stilbene. These results can be explained in two ways: either the original mercury compound has the same configuration as the stilbene that it yields, or in the reaction

$$C_6H_5CH = C(HgX)C_6H_5 + HCl \longrightarrow C_6H_5CH = CHC_6H_5$$

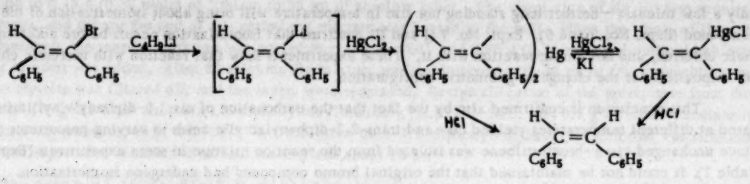
complete reversal of configuration occurs for both isomers. It is more likely that the configuration is retained.

From all these results it may be inferred with a considerable amount of confidence that the substance of m.p. 141-142° is trans-1,2-diphenylvinylmercury chloride, the substance of m.p. 130-131° being its cis isomer, and the

* The absorption spectra were determined for us by T. N. Shkurina at the Optical Laboratory of the Institute of Organic Chemistry.

substance of m.p. 243-244° is trans-bis (1,2-diphenylvinyl)mercury, the substance of m.p. 145-147° being its cis isomer.

Thus, starting from cis- and trans-α-bromostilbenes we have carried out two series of reactions:



(and similarly for the trans isomer).

In all of these reactions the replacement occurs at the olefin carbon responsible for the geometric configuration, and all of these reactions are stereochemically pure, i.e. proceed with retention of the original geometric configuration. In other words, this series of reactions provides confirmation of the rule relating to the retention of geometric configuration in electrophilic and radical exchange reactions [7].

An apparent exception is the reaction in which 1,2-diphenylvinyllithium is formed, for we have shown that, by variation in the temperature and duration of reaction during the formation of the lithium reagent, it is possible to obtain trans-bis(1,2-diphenylvinyl)mercury (m.p. 243-244°) from cis-α-bromostilbene. We have succeeded in showing, however, that the change in geometric configuration does not occur at the moment of reaction, but is due to isomerization of the cis-1,2-diphenylvinyllithium. This was proved in a special series of experiments, the results of which are given in Table 1.

TABLE 1

Expt. No.	Molar ratio of cis bromo cpd. to C_4H_9Li	Temperature of reaction with C_4H_9Li(°C)	Duration of reaction with C_4H_9Li (min)	Molar ratio of cis bromo cpd. to $HgCl_2$	Temperature of reaction with $HgCl_2$(°C)	Duration of reaction with $HgCl_2$ (min)	Yield of trans R_2Hg •• (%)	Yield of cis- R_2Hg (%)	Yield of cis- RHgCl (%)
1	1:1.25	(−40)−(−35)	10	2:1	(−40)−(−35)	15	−	50	−
2	1:1.5	(−30)−(−15)	7	2:1	(−40)−(−35)	30	24	21	−
3	1:1.25	(−40)−(−35)	40	2:1	(−40)−(−35)	15	24	22	−
4	1:1.3	(−30)−(−15)	60	2:1	(−30)−(−10)	30	70	−	−
5•	1:1.5	(−40)−(−35)	11	2:1	At first (−40)−(−35), later +15	10	−	43	−
6	1:1.25	(−40)−(−35)	7	2:1	At first (−40)−(−35), later 16−18	10 12 hours	−	31	−
7	1:1.25	(−20)−(−10)	30	2:1	I. (−20)−(−10) II. (−40)−(−35)	30 20	47 43	− −	− −
8	1:1.25	(−40)−(−35) ½ reaction mixture	10	1:1	(−40)−(−35)	30	−	−	40
9	1:1.25	(−40)−(−35) ½ reaction mixture	10	2:1	(−40)−(−35)−	20	−	51	−
		At first (−40)−(−35) later (−15)−(−10)	10 20	2:1	(−40)−(−35)−	20	48	−	−

• In Expt. No. 5 unchanged cis-α-bromostilbene was isolated.

•• R is $C_6H_5CH=CC_6H_5$.

It will be seen from these results that variations in reaction temperature and time for the stage in which the lithium compound is formed have considerable effects on the yields of cis and trans mercury compounds (Expts. 1, 2, 3 and 4). On the other hand, when reaction with mercuric chloride is complete – which requires only a few minutes – neither long standing nor rise in temperature will bring about isomerization of the mercury compound (Expt. No. 5 and 6). Expt. No. 7 (I and II) confirms that isomerization occurs before addition of mercuric chloride, and not during reaction with it. These experiments show that reaction with mercuric chloride is not responsible for the change in geometric configuration.

This conclusion is confirmed also by the fact that the carbonation of cis-1,2-diphenylvinyllithium prepared at different temperatures yielded cis- and trans-2,3-diphenylacrylic acids in varying proportions (Table 2). Since unchanged cis-α-bromostilbene was isolated from the reaction mixture in some experiments (Expt. No. 5, Table 1), it could not be maintained that the original bromo compound had undergone isomerization.

TABLE 2

Expt. No.	Molar ratio of cis bromo compound to C_4H_9Li	Temperature of reaction with C_4H_9Li (°C)	Duration of reaction with C_4H_9Li (min)	Yield of cis-2,3-diphenylacrylic acid (%)	Yield of trans-2,3-diphenylacrylic acid (%)
1	1 : 1.25	(– 40) – (– 35)	11	61	–
2	1 : 1.25	(– 20) – (– 10)	11	15	30
3	1 : 1.25	(– 20) – (– 10)	40	–	58

It now remains to be decided whether the change of configuration occurs in the moment of reaction between butyllithium and cis-α-bromostilbene, or whether it is the cis-1,2-diphenylvinyllithium so prepared that undergoes isomerization.

It may be inferred from the results of Expt. No. 9 that the exchange of bromine for lithium occurs without change of configuration, but that cis-1,2-diphenylvinyllithium is a very unstable substance, which, even at – 40° can exist for only 10-15 minutes, and is isomerized completely at –15°. On account of its low stability, cis-1,2-diphenylvinyllithium cannot be prepared by reaction of cis-α-bromostilbene with lithium, since this reaction requires a temperature of 16 - 18°.

It is difficult to say whether the isomerization of cis-1,2-diphenylvinyllithium results solely from thermal action or whether there is also some other factor, for we have not obtained the lithium compound in a pure state. Its instability is somewhat unexpected, for the temperature at which cis-trans conversion occurs is 180-200° for stilbene itself [16], 200° for cis-α-bromostilbene [15], and 140-160° for the mercury derivative of cis-stilbene that we have synthesized (m.p. 145 - 147°). It will be seen from the results given in Table 1 that reaction of cis-1,2-diphenylvinyllithium with mercuric chloride does not always yield the symmetrical mercury compound. Under some conditions the sole product may be cis-1,2-diphenylvinylmercury chloride (Expt. No. 8).

EXPERIMENTAL

1. Preparation of trans-Bis(1,2-diphenylvinyl)mercury

All experiments on the reaction of trans-1,2-diphenylvinyllithium with mercuric chloride were carried out in an apparatus provided with stirrer, condenser, dropping funnel, tube for passage of gas, and thermometer immersed in the reaction mixture. A current of dry pure nitrogen was passed through the apparatus.

1) At a temperature of – 30° to – 20° a titrated solution of butyllithium (0.0125 mole) was added to a solution of 3 g (0.01 mole) of trans-α-bromostilbene in 24 ml of benzene and 36 ml of ether (all solvents were carefully purified and dried). The mixture was stirred for 40 minutes, and 1.5 g (0.005 mole) of mercuric chloride was then added at – 30° to – 20°. The mixture was stirred vigorously for a further 40 minutes, and was then decomposed with 50 ml of 5% hydrochloric acid. The precipitate of trans-bis(1,2-diphenylvinyl)mercury was filtered off, and the layers were separated. The yield of trans-bis(1,2-diphenylvinyl)mercury was 2 g (62%). After two recrystallizations from dioxan the product melted at 243-244°, and further recrystallizations did not affect the melting point. A very small amount of trans-1,2-diphenylvinylmercury chloride (m.p. after recrystallization from alcohol 139.5-140.5°) was isolated from the ether-benzene layer after removal of solvent, and at the same time 1 g (33% of the amount taken) of unchanged trans-α-bromostilbene was obtained.

Trans-bis(1,2-diphenylvinyl)mercury is almost insoluble in alcohol, ether, petroleum ether, chloroform, and acetone, is of low solubility in benzene, and is moderately soluble in dioxan and xylene.

		Found %	C 59.73; 59.70;	H 3.69; 3.96;	Hg 35.78; 35.71
$C_{28}H_{22}Hg$.		Calculated %	C 60.15;	H 3.96;	Hg 35.88

2) A solution of 2.5 g (0.01 mole) of trans-α-bromostilbene in 10 ml of ether was added at room temperature to 0.15 g (0.02 mole) of lithium in 35 ml of absolute ether. The dissolution of the lithium required four hours, and toward the end of this period the mixture was heated to the boil. When the whole of the lithium had dissolved, the reaction mixture was cooled to −30° to −20°, and 2.65 g (0.01 mole) of mercuric chloride in 80 ml of ether was added. After 30 minutes the mixture was decomposed with 50 ml of 5% hydrochloric acid, the precipitate was filtered off, and the layers were separated. Recrystallization of the precipitate from dioxan yielded 0.75 g (29%) of trans-bis(1,2-diphenylvinyl)mercury, m.p. 239-241°, and 0.5 g of trans-1,2-diphenylvinylmercury chloride, m.p. 141-142°. A little more trans-1,2-diphenylvinylmercury chloride was obtained from the the ether layer after removal of solvent (total yield about 13%).

2. Reaction of trans-Bis(1,2-diphenylvinyl)mercury with Mercuric Chloride

A mixture of 1.45 g of trans-bis(1,2-diphenylvinyl)mercury, 0.8 g of mercuric chloride, and 25 ml of absolute alcohol was heated for 5 hours 30 minutes in a sealed tube in a boiling water bath. The tube was then opened, and the crystals present were filtered off. The product was 2.05 g (93%) of trans-1,2-diphenylvinylmercury chloride, m.p. 137-139°. One recrystallization from alcohol raised the melting point to 141.5-142°, but further recrystallizations did not raise it beyond this value.

This substance is readily soluble in alcohol, chloroform, and dioxan, moderately soluble in benzene, somewhat soluble in ether, and insoluble in petroleum ether.

		Found %	C 40.31; 40.48;	H 2.88; 2.71;	Hg 48.15
$C_{14}H_{11}ClHg$		Calculated %	C 40.48;	H 2.67;	Hg 48.30

3. Decomposition of trans-Bis(1,2-diphenylvinyl)mercury and of trans-1,2-Diphenylvinylmercury Chloride with Hydrochloric Acid.

1) A mixture of 1 g of trans-bis(1,2-diphenylvinyl)mercury and 30 ml of hydrochloric acid (1 : 1) was refluxed for one hour. The reaction mixture was then extracted with ether, and the ether was removed from the extract. The product was 0.6 g (95%) of trans-stilbene, m.p. 123-124° after a single recrystallization from alcohol. There was no depression in a mixture test with an authentic sample.

2) Trans-1,2-Diphenylvinylmercury chloride (3 g) was decomposed with 50 ml of HCl (1 : 1) under the same conditions. The product was 1.25 g (96%) of trans-stilbene, m.p. 122-123.5°.

4. Symmetrization of trans-1,2-Diphenylvinylmercury Chloride

1) Symmetrization with Potassium Iodide. A solution of 4 g (0.024 mole) of potassium iodide in 62 ml of acetone and 7 ml of water was added to a solution of 1 g (0.0024 mole) of trans-1,2-diphenylvinylmercury chloride in a mixture of 50 ml of acetone and 5 ml of water. A precipitate of fine needles began to form immediately. The mixture was set aside for one day at room temperature, and the precipitate was then filtered off. The product was 0.55 g (85%) of trans-bis(1,2-diphenylvinyl)mercury, which melted at 243-244° after one recrystallization from dioxan and showed no depression in a mixture melting test with the trans-bis(1,2-diphenylvinyl)mercury obtained from the lithium reagent.

2) Symmetrization with Butyllithium. A solution of 1 g of trans-1,2-diphenylvinylmercury chloride in a mixture of 40 ml of benzene and 60 ml of ether was cooled to −40° to −30° and, in an atmosphere of nitrogen, an equimolecular amount of a titrated ethereal solution of butyllithium was added. A precipitate began to appear immediately. The mixture was allowed to stand at the same temperature for 40 minutes, and was then decomposed with 50 ml of 3% hydrochloric acid. The precipitate of trans-bis(1,2-diphenylvinyl)mercury was filtered off, and the layers were separated. The yield of trans-bis(1,2-diphenylvinyl)mercury was 0.5 g (83%). It melted at 239-241° and showed no melting point depression in admixture with the sample obtained with the aid of the lithium reagent. A very small amount of trans-1,2-diphenylvinylmercury chloride, m.p. 139-141°, was isolated from the ether-benzene layer.

5. Preparation of cis-Bis(1,2-diphenylvinyl)mercury

The preparation of cis-bis(1,2-diphenylvinyl)mercury was carried out in the apparatus used for the preparation of the trans isomer. A titrated ethereal solution of butyllithium (0.025 mole was added at −40° to −35° to a solution of 5 g (0.02 mole) of cis-α-bromostilbene in a mixture of 40 ml of benzene and 60 ml of ether. Care was taken that the temperature did not exceed −35°. After a period of ten minutes from the beginning of the addition

of butyllithium, 2.55 g (0.01 mole) of mercuric chloride in 200 ml of ether was added to the solution of lithium reagent, the temperature being constantly maintained at −40° to −35°. The reaction with mercuric chloride was complete in 10-15 minutes, its completion being marked by the disappearance of the dark color characteristic of the lithium reagent. A completely clear light-yellow solution was obtained. It should be noted that the lithium chloride formed in the reaction was not precipitated; it probably formed a soluble complex. The reaction mixture was decomposed with 50 ml of 3% hydrochloric acid, and the layers were separated. The ether-benzene layer, after removal of solvent, yielded 2.7 g (50%) of cis-bis(1-2, diphenylvinyl)mercury, m.p. 145-147° after two recrystallizations from a mixture of benzene and alcohol. Further recrystallizations did not affect the melting point.

cis-Bis(1,2-diphenylvinyl)mercury is highly soluble in benzene and moderately soluble in alcohol and chloroform. A mixture with trans-bis(1,2-diphenylvinyl)mercury melted over the range 140-220°.

	Found %	C 59.80; 59.92;	H 4.18; 4.05;	Hg 35.69
$C_{28}H_{22}Hg$.	Calculated %	C 60.15;	H 3.96;	Hg 35.88

6. Preparation of cis-1,2-Diphenylvinylmercury Chloride

cis-α-Bromostilbene (5 g, i.e. 0.02 mole) was caused to react with butyllithium (0.025 mole) under the conditions described for the preceding experiment. Mercuric chloride (5.2 g, i.e. 0.02 mole) was then added, without solvent, to the reaction mixture. Reaction was allowed to proceed for 30 minutes, and the mixture was then treated as in the preceding experiment. A small amount (14%) of trans-bis(1,2-diphenylvinyl)mercury, m.p. 240-241°, was obtained, and the main product was 3.1 g (40%) of cis-1,2-diphenylvinylmercury chloride, m.p. 130-131° after two recrystallizations from alcohol. Further recrystallizations did not affect the melting point.

cis-1,2-Diphenylvinylmercury chloride is readily soluble in alcohol and chloroform, but somewhat less soluble in benzene.

	Found %	C 40.28; 40.44	H 2.71; 2.77;	Hg 48.42; 48.40
$C_{14}H_{11}ClHg$.	Calculated %	C 40.48;	H 2.67	Hg 48.30

7. Decomposition of cis-Bis(1,2-diphenylvinyl)mercury and of cis-1,2-Diphenylvinylmercury Chloride with Hydrochloric Acid.

1) A mixture of 2 g of cis-bis(1,2-diphenylvinyl)mercury and 40 ml of HCl (1 : 1) was heated for 30 minutes, and was then extracted with ether. The oily liquid remaining after removal of ether was heated for 40 minutes at 180-200°. The product was 1.2 g (92%) of trans-stilbene, m.p. 123-124° after one recrystallization from alcohol. The melting point was undepressed by admixture of authentic material.

2) cis-1,2-Diphenylvinylmercury chloride (3 g) was decomposed with 50 ml of HCl under the same conditions, and yielded a noncrystallizing oil of cis-stilbene, which was isomerized to the trans isomer as described above. The product was 1.25 g (96%) of trans-stilbene, m.p. 122-123°, undepressed by admixture of authentic material.

8. Reaction of cis-α-Bromostilbene with Lithium

The reaction of cis-α-bromostilbene with lithium was carried out under the conditions used for the trans isomer, but the reaction temperature was lowered to 16-18°. The products obtained from 5 g of cis-α-bromostilbene were 0.85 g (10%) of trans-bis(1,2-diphenylvinyl)mercury, m.p. 242-244°, and 1.3 g (25%) of trans-1,2-diphenylvinylmercury chloride, m.p. 141-141.5°.

9. Carbonation of cis-1,2-Diphenylvinyllithium

cis-1,2-Diphenylvinyllithium, prepared under various temperature conditions, was subjected to carbonation with solid carbon dioxide. The reaction mixture was decomposed with 3% hydrochloric acid and extracted with benzene. Aniline was added to the dried benzene solution, and trans-2,3-diphenylacrylic acid was precipitated as its aniline salt, m.p. 127-129° (the literature [12] gives 129°). The filtrate was treated with 15% aqueous caustic potash, and acidification of the solution yielded cis-2,3-diphenylacrylic acid, m.p. 172-173° (the literature [12] gives 174-175°). The experimental results are given in Table 2.

10. Symmetrization of cis-1,2-Diphenylvinylmercury Chloride

1) Symmetrization with Potassium Iodide. A solution of 4 g (0.024 mole) of potassium iodide in a mixture of 60 ml of acetone and 7 ml of water was added to a solution of 1 g (0.0024 mole) of cis-1,2-diphenylvinylmercury chloride in 50 ml of acetone. The mixture stood at room temperature for two days. The small amount of inorganic precipitate was filtered off, and some of the acetone was driven off the filtrate under reduced pressure. When the solution was cooled, crystals appeared, and 0.35 g (52%) of cis-bis(1,2-diphenylvinyl)mercury was obtained; it melted

at 145-147° after recrystallization from a mixture of alcohol and chloroform, and the melting point was not depressed by admixture of material prepared from cis-1,2-diphenylvinyllithium. The residue remaining after complete removal of acetone was treated with boiling benzene and, as a result, 0.2 g of the original cis-1,2-diphenylvinylmercury chloride, m.p. 130-131°, was isolated.

2) Symmetrization with Butyllithium. A solution of 1 g of cis-1,2-diphenylvinylmercury chloride in a mixture of 40 ml of benzene and 60 ml of ether was cooled to −40° to −30°, and, at this temperature in an atmosphere of nitrogen, an equimolecular amount of a titrated ethereal solution of butyllithium was added. The mixture, which remained completely clear, was allowed to stand at −40° to −30° for 40 minutes. It was then decomposed with 50 ml of 3% hydrochloric acid, the layers were separated, and the ether-benzene layer was dried with calcium chloride. The solvent was removed under reduced pressure, and the residue yielded 0.4 g (66%) of cis-bis(1,2-diphenylvinyl)-mercury, m.p. 145-147° after one recrystallization from a mixture of alcohol and benzene. A mixture test with a sample prepared via the lithium reagent showed no depression.

11. Reaction of cis-Bis(1,2-diphenylvinyl)mercury with Mercuric Chloride

A mixture of 1 g of cis-bis(1,2-diphenylvinyl)mercury, 0.5 g of mercuric chloride, and 40 ml of absolute alcohol was heated in a sealed tube for five hours in a boiling water bath. The tube was then opened, and the crystals that had formed were filtered off. The product was 1.1 g (79%) of cis-1,2-diphenylvinylmercury chloride, m.p. 130-131° after recrystallization from alcohol. A mixture test with a sample prepared via cis-1,2-diphenylvinyllithium showd no depression. After removal of solvent about 0.1 g of unchanged cis-bis(1,2-diphenylvinyl)mercury was isolated.

12. Ultraviolet Irradiation of cis-Bis(1,2-diphenylvinyl)mercury

A solution of 1 g of cis-bis(1,2-diphenylvinyl)mercury in 50 ml of chloroform was exposed to the radiation from a PRK-4 quartz lamp for three hours. Already after 30 minutes a precipitate of fine needles began to appear, and this precipitate had become appreciable by the end of the three hours, when it was filtered off. The product was 0.50 g (50%) of trans-bis(1,2-diphenylvinyl)mercury, and without recrystallization it melted at 243-244°, undepressed by admixture of an authentic sample. After removal of chloroform, 0.3 g (30% of the amount taken) of unchanged cis-bis-(1,2-diphenylvinyl)mercury was separated. A slight deposit of univalent mercury salt formed on the walls of the flask.

It was not found possible to convert trans isomers of mercury derivatives of stilbene into their cis isomers. Prolonged ultraviolet irradiation destroyed the substances investigated, but did not convert them into cis modifications.

13. Thermal Isomerization of cis-Bis(1,2-diphenylvinyl)mercury

cis-Bis(1,2-diphenylvinyl)mercury (0,5 g) was heated at 140-160° in a sealed tube for four hours. In the course of this treatment mercury separated at the bottom of the tube. After the heating the contents of the tube were treated successively with benzene and dioxan. From the dioxan 0,25 g (50%) of trans-bis(1,2-diphenylvinyl)mercury, m.p. 242-244°, was separated; it showed no depression in a mixture test with an authentic sample. From the benzene 0,1 g of trans-stilbene, m.p. 121-122°, was separated, and its melting point was not depressed by admixture of authentic stilbene.

SUMMARY

1. By treatment of the geometric isomers of 1,2-diphenylvinyllithium with mercuric chloride, the stereoisomeric bis(1,2-diphenylvinyl)mercurys have been prepared.

2. By the disymmetrization of the stereoisomeric bis(1,2-diphenylvinyl)mercurys, the stereoisomeric 1,2-diphenylvinyl mercury chlorides have been prepared.

3. An investigation has been made of the symmetrization of the stereoisomeric 1,2-diphenylvinylmercury chlorides with formation of the original bis(1,2-diphenylvinyl)mercurys.

4. A study has been made of the conditions required for the isomerization of cis-1,2-diphenylvinyllithium and of cis-bis(1,2-diphenylvinyl)mercury into the corresponding trans isomers.

5. It has been shown that the investigated exchange reactions occurring at the olefin carbon responsible for geometric isomerism are stereochemically pure and occur without change in the original configuration.

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Received February 13, 1954

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ALKYLATION AND ACYLATION OF (CHLOROMERCURI)ACETALDEHYDE

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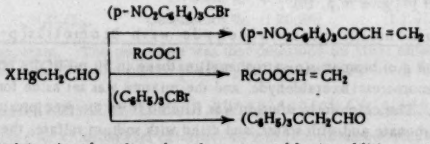
One of the present authors and Lutsenko have already pointed out the dual reactivity of α-mercurated aldehydes and ketones [1, 2, 3]. Thus, when (chloromercuri)acetaldehyde, (chloromercuri)acetone, and 2-(chloromercuri)acetophenone react with chlorotriphenylmethane, the respective products are triphenylmethyl derivatives of acetaldehyde, acetone, and acetophenone; i.e., C-alkylation occurs. When these mercury carbonyl compounds react with acetyl chloride and benzoyl chloride, however, the corresponding vinyl esters of acetic and benzoic acids are formed; i.e., O-alkylation occurs [2]. Further study of the way in which the direction of the reaction (reaction at C or at O) depends on the structure of the alkylating or acylating reagent demands examination of the behavior of a larger number of reagents.

We now describe a study of the reactions of mercurated acetaldehyde with bromotriphenylmethane, with bromotris(p-nitrophenyl)methane, with p-nitrobenzoyl chloride, with chloroacetyl chloride, with trichloroacetyl chloride, with triphenylacetyl chloride, and with phthalimidoacetyl chloride. All of the acid chlorides investigated, irrespective of their structure, reacted with (chloromercuri)acetaldehyde with formation of the corresponding vinyl esters in 40-58% yield. The structures of the resulting vinyl esters, which, apart from vinyl chloroacetate, have not been described in the literature, were established by acid hydrolysis. Acetaldehyde was identified as its p-nitrophenylhydrazone, and the acids were identified by their melting points; the phenacyl derivatives of chloroacetic and trichloroacetic acids were prepared.

Bromotriphenylmethane behaved like chlorotriphenylmethane [2] in its reaction with (bromomercuri)acetaldehyde, triphenylmethyl-substituted acetaldehyde (3,3,3-triphenylpropionaldehyde) being formed; no triphenylmethyl vinyl ether was formed. The identity of the 3,3,3-triphenylpropionaldehyde was proved by preparing its p-nitrophenylhydrazone, and by the absence of depression in a mixture melting test with the 3,3,3-triphenylpropionaldehyde prepared by the ozonization of 4,4,4-triphenyl-1-butene, which was prepared from chlorotriphenylmethane and allyl chloride.

Bromotris(p-nitrophenyl)methane behaved like the acid chlorides in its reaction with (bromomercuri acetaldehyde. This reaction provides a convenient method for the synthesis of the vinyl ether of tris(p-nitrophenyl)methanol, which has not been described previously.



The structure of the vinyl ether of tris(p-nitrophenyl)methanol was proved by its addition reaction with bromine, the absence of reactions for aldehydes, and the formation of tris(p-nitrophenyl)methanol by acid hydrolysis.

Alkyl halides, including even such compounds as allyl chloride and benzyl chloride, did not react with mercurated acetaldehyde. The alkylation reaction was given only by bromotriphenylmethane (which reacted like chlorotriphenylmethane [2], which yielded 3,3,3-triphenylpropionaldehyde. Intensification of the electrophilic character of the reagent by the introduction of three nitro groups [bromotris(p-nitrophenyl)methane] led to a change in the direction of the reaction. Bromotris(p-nitrophenyl)methane reacted like the acid chlorides and gave a vinyl ether. Picryl chloride did not react with mercurated acetaldehyde. Owing to the selective reactivity of mercurated acetaldehyde toward halogen compounds, the choice of alkylating reagents is limited.

Thus, in all of the examples studied of the acylation of mercurated acetaldehyde, reaction is at the oxygen atom, i.e., occurs with transfer of the reaction center along the conjugated system of Hg—C and C=O bonds, whereas alkylation, depending on the reagent, may occur either with or without transfer of reaction center.

EXPERIMENTAL

Reaction of (Bromomercuri)acetaldehyde with Bromotriphenylmethane

A solution of 3 g of bromotriphenylmethane in 25 ml of absolute benzene was added to 3 g of dry, carefully

ground (bromomercuri)acetaldehyde that had not been recrystallized. The mixture was heated for two hours at 50-60° and for two hours at the boil. The precipitate was then filtered off, and the benzene was distilled off. The product was 2.4 g of crude 3,3,3-triphenylpropionaldehyde melting at 85-95°, and 2.0 g of this was recrystallized several times, first from ligroin, and then from methanol. The 3,3,3-triphenylpropionaldehyde so obtained (0.9 g) melted at 99-100.5°, and there was no depression in a mixture test with 3,3,3-triphenylpropionaldehyde obtained by the ozonization of 4,4,4-triphenyl-1-butene (mixture melted at 99-100.5°). The p-nitrophenylhydrazone of 3,3,3-triphenylpropionaldehyde, m.p. 245-246°, was recrystallized from toluene.

	Found %:	N 10.25; 10.17
$C_{27}H_{23}N_3O_2$.	Calculated %:	N 9.97

To a solution of 0.3 g of crude 3,3,3-triphenylpropionaldehyde in 1 ml of chloroform, 2 ml of a chloroform solution of 0.028 g of bromine was added. The color of the solution, as judged by comparison with a standard color, did not change over a period of five minutes. Hence, no triphenylmethyl vinyl ether was formed in the reaction of bromotriphenylmethane with mercurated acetaldehyde.

Preparation of 4,4,4-Triphenyl-1-butene(allyltriphenylmethane). A solution of 3 g of allyl chloride in 100 ml of absolute ether was added gradually with vigorous mechanical stirring to 10 g of magnesium that had been activated with iodine, and to the mixture so obtained a solution of 17 g of chlorotriphenylmethane and 10 g of allyl chloride in 250 ml of absolute ether was added slowly. The reaction mixture was heated with constant stirring for six hours, and was then decomposed with dilute hydrochloric acid. The product was 12 g (70%) of 4,4,4-triphenyl-1-butene, m.p. 70.5-71° (recrystallized from methanol).

	Found %:	C 92.91; 92.79; H 7.15; 7.15
$C_{22}H_{20}$.	Calculated %:	C 92.91; H 7.09;

Ozonization of 4,4,4-Triphenyl-1-butene. Ozonized oxygen (0.042 g of ozone per liter) was passed for ten hours through a solution of 7 g of 4,4,4-triphenyl-1-butene in 50 ml of chloroform. The chloroform was driven off under reduced pressure at 26°, and the oil that remained was treated with water, first in the cold, and then with heating. It was then dissolved in ether, and the solution was washed with water, with 5% caustic soda solution, and again with water. It was dried with sodium sulfate, and the ether was driven off. The residue crystallized out when petroleum ether was added. Two recrystallizations (from petroleum ether and from methanol) yielded 3 g of 3,3,3-triphenylpropionaldehyde, m.p. 98.5-100°. The yield was 43%.

	Found %:	C 87.96; 88.12; H 6.44; 6.28
$C_{21}H_{18}O$.	Calculated %:	C 88.08; H 6.33;

Hellerman and Garner [4] give m.p. 101°.

Reaction of (Bromomercuri)acetaldehyde with Bromotris(p-nitrophenyl)methane

A solution of 3.8 g of bromotris(p-nitrophenyl)methane in 50 ml of dry chloroform was mixed with 3.8 g of carefully ground (bromomercuri)acetaldehyde, and the mixture was set aside for two days and then heated for three hours in a water bath. The chloroform solution was filtered from the precipitate, washed several times with a 10% solution of sodium carbonate and with water, and dried with sodium sulfate; the chloroform was distilled off. Recrystallization from acetone yielded 1.4 g (40%) of tris(p-nitrophenyl)methyl vinyl ether, m.p. 164-164.5°(with decomposition).

	Found %:	C 60.12; 60.25; H 3.61; 3.74
$C_{21}H_{15}N_3O_7$	Calculated %:	C 59.85; H 3.59

Tris(p-nitrophenyl)methyl vinyl ether decolorizes a chloroform solution of bromine and does not react with hydroxylamine and p-nitrophenylhydrazine. It is hydrolyzed by hydrochloric acid with formation of tris(p-nitrophenyl)-methanol.

Bromotris(p-nitrophenyl)methane was prepared by heating 6 g of tris(p-nitrophenyl)methane with 4 g of dry bromine at 100-102° in a sealed tube for ten hours. The excess of bromine was absorbed by caustic alkali in a vacuum desiccator, and the bromotris(p-nitrophenyl)methane was then washed with ether and boiled with a small amount of benzene to remove residual bromine. The yield was 5.9 g (82%); m.p. 188-190°.

Data in the literature: Ziegler and Boye [5]; decomposition temperature 191°; Lewis, Lipkin, and Magel [6]; m.p. 189.9-190.9°; Leffler [7]; m.p. 200-200.5°.

Hydrolysis of Tris(p-nitrophenyl)methyl Vinyl Ether. A chloroform solution of 0.2 g of tris(p-nitrophenyl)-methyl vinyl ether was heated for 30 minutes with 10 ml of concentrated hydrochloric acid. The product was 0.06 g (84%) of tris(p-nitrophenyl)methanol, which melted at 188-190° after several recrystallizations from benzene. A mixture melting test with authentic tris(p-nitrophenyl)methanol gave no depression (m.p. 189-191°).

Reaction of (Chloromercuri)acetaldehyde with Chloroacetyl Chloride

A solution of 19 g of chloroacetyl chloride in 15 ml of benzene was added to a suspension of 50 g of dry, carefully ground, crude (not recrystallized*) (chloromercuri)acetaldehyde in 45 ml of absolute benzene. The mixture was shaken until no further rise in temperature occurred; and it was then heated at 60-70° for two hours and at the boil for two hours. The precipitate was filtered off and washed with benzene, and excess of benzene was driven off. Two distillations through a 28-cm Burpé fractionating column yielded 10.6 g (58%) of vinyl chloroacetate, b.p. 134.5-135.5° (771 mm); 62-63.5° (58 mm); n_D^{20} 1.4460; d_4^{20} 1.1941; MR 26.89; $C_4H_5O_2ClF$. Calculated MR 26.73.

	Found %:	C 39.95; 40.02;	H 4.33; 4.27
$C_4H_5O_2Cl$.	Calculated %:	C 39.91	H 4.09

Wiley [8] gives b.p. 37-38° (16 mm); n_D^{25} 1.4422.

The solid residue from the distillation was extracted with benzene, and the benzene was distilled off. Chloroacetic acid, m.p. 56-57°, was obtained; there was no depression in a mixture test (57-59°).

Hydrolysis of Vinyl Chloroacetate. A mixture of 0.64 g of vinyl chloroacetate and 25 ml of 20% sulfuric acid was boiled for 30 minutes. The acetaldehyde evolved was trapped in a solution of 0.81 g of p-nitrophenylhydrazine in 100 ml of 15% acetic acid, and 0.8 g (80%) of acetaldehyde p-nitrophenylhydrazone was obtained. After recrystallization from 50% alcohol it melted at 123-125°, and there was no depression in a mixture test (124-125°).

The aqueous solution of sulfuric and chloroacetic acids that remained in the flask after removal of acetaldehyde was neutralized with caustic soda. The solution was then rendered acid to litmus by addition of one drop of sulfuric acid, and a solution of 0.5 g of 2-bromoacetophenone in 10 ml of alcohol was added. The mixture was refluxed for one hour, and 0.25 g (47%) of phenacyl chloroacetate was obtained, melting at 94-95° after recrystallization from alcohol. A mixture with the phenacyl ester obtained from pure chloroacetic acid (m.p. 96°) melted without depression (95-96°).

Reaction of (Chloromercuri)acetaldehyde with Trichloroacetyl Chloride

The procedure was that described for chloroacetyl chloride: 46 g of (chloromercuri)acetaldehyde and 27 g of trichloroacetyl chloride yielded 14 g (53%) of vinyl trichloroacetate, b.p. 67-68° (42 mm); n_D^{28} 1.4670; d_4^{20} 1.4147; MR_D 37.24; $C_4H_3O_2Cl_3F$; Calculated: MR 36.46.

	Found %:	C 25.48; 25.31;	H 1.74; 1.72
$C_4H_3O_2Cl_3$.	Calculated %:	C 25.36;	H 1.61

Hydrolysis of Vinyl Trichloroacetate. The procedure was that described for vinyl chloroacetate. The yield of acetaldehyde p-nitrophenylhydrazone was 73%, and that of phenacyl trichloroacetate (m.p. 49-50°) was 52%. Mixture tests were undepressed.

Reaction of (Chloromercuri)acetaldehyde with Phenylacetyl Chloride

The procedure was that described for chloroacetyl chloride: 44 g of (chloromercuri)acetaldehyde and 22 g of phenylacetyl chloride yielded 14.2 g (50%) of vinyl phenylacetate, b.p. 80-81° (2 mm); n_D^{26} 1.5163; d_4^{20} 1.0533; MR 46.51. $C_{10}H_{10}O_2F_4$. Calculated %: MR 45.97.

	Found %:	C 74.07; 74.00;	H 6.44 6.42
$C_{10}H_{10}O_2$.	Calculated %:	C 74.05;	H 6.22

Hydrolysis of Vinyl Phenylacetate. The procedure was that described for vinyl chloroacetate, 1.8 g of the ester being boiled with 20% sulfuric acid for 1 hour 30 minutes. The yield of acetaldehyde p-nitrophenylhydrazone, m.p. 124-126°, was 1.4 g (67%), and a mixture test was not depressed (124-126°). The yield of phenylacetic acid, m.p. 72-74°, was 1.2 g (80%), and again a mixture test was not depressed (73-75°).

Reaction of (Chloromercuri)acetaldehyde with Triphenylacetyl Chloride

The procedure was that described for chloroacetyl chloride. The benzene was distilled off, and the residue was treated with ligroin, the insoluble part being filtered off and recrystallized several times from alcohol. It was then dissolved in hot benzene and precipitated with petroleum ether. A yield of 0.5 g (48%) of vinyl triphenylacetate, m.p. 126.5-127.5°, was obtained from 0.9 g of triphenylacetyl chloride and 1 g of (chloromercuri)acetaldehyde.

* The reaction goes better with (chloromercuri)acetaldehyde that has not been recrystallized.

	Found %:	C 84.05; 84.16;	H 5.83; 5.95
$C_{22}H_{18}O_2$.	Calculated %:	C 84.05;	H 5.78

Vinyl triphenylacetate is readily soluble in benzene, chloroform, hot alcohol, and hot ligroin. It is stable in the air.

Hydrolysis of Vinyl Triphenylacetate. The vinyl ester (0.8 g) was boiled for one hour with a mixture of 5 ml of 65% sulfuric acid, 5 ml of water, and 10 ml of dioxan. The yield of acetaldehyde p-nitrophenylhydrazone was 0.12 g (42%). The residue in the flask was poured into 100 ml of cold water. The precipitate was filtered off and treated with 120 ml of a hot 10% solution of caustic potash. The insoluble part (0.3 g) - which was vinyl triphenylacetate, since a mixture test with the original substance showed no depression - was filtered off. The yield of triphenylacetic acid was 0.4 g (87% on the amount of ester that reacted). After recrystallization from alcohol it melted at 263-265°, and a mixture test was undepressed.

Reaction of (Chloromercuri)acetaldehyde with p-Nitrobenzoyl Chloride •

The procedure was that described for chloroacetyl chloride. The benzene solution was washed with 5 % caustic soda solution and with water, and was dried with sodium sulfate. The benzene was distilled off, and the residue was recrystallized from alcohol. A yield of 4.3 g (55%) of vinyl p-nitrobenzoate, m.p. 69.5-70.5°, was obtained from 7.5 g of p-nitrobenzoyl chloride and 12.5 g of (chloromercuri)acetaldehyde.

	Found %:	C 55.79; 55.90;	H 4.02; 4.07;	N 7.53; 7.61
$C_9H_7NO_4$.	Calculated %:	C 55.86;	H 3.66;	N 7.26

Hydrolysis of Vinyl p-Nitrobenzoate. The procedure was that described for vinyl chloroacetate, and 0.35 g of the vinyl ester yielded 0.26 g (81%) of acetaldehyde p-nitrophenylhydrazone and 0.18 g (60%) of p-nitrobenzoic acid, m.p. 235-236°. Mixture tests were undepressed.

Reaction of (Chloromercuri)acetaldehyde with Phthalimidoacetyl Chloride •

The procedure was that described for chloroacetyl chloride: 2 g of phthalimidoacetyl chloride and 2.75 g of (chloromercuri)acetaldehyde yielded 0.8 g (40%) of vinyl phthalimidoacetate, m.p. 104-105° after recrystallization from ligroin.

	Found %:	62.51; 62.55;	H 3.89; 4.07;	N 5.86; 5.87
$C_{12}H_9NO_4$.	Calculated %:	62.34;	H 3.90;	N 6.06

Hydrolysis of Vinyl Phthalimidoacetate. The procedure was that described for vinyl chloroacetate: 0.45 g of the vinyl ester yielded 0.2 g (57%) of phthalimidoacetic acid, m.p. 192° after recrystallization from water. A mixture test was not depressed.

SUMMARY

1. It has been shown that the reaction of mercurated acetaldehyde with carboxylic acid chlorides results in the formation of the corresponding vinyl esters; In a similar way, bromotris(p-nitrophenyl)methane yields the corresponding vinyl ether. In these reactions transfer of reaction center along the system of conjugated Hg–C and C=O bonds occurs.

2. It has been shown that the reaction of mercurated acetaldehyde with bromotriphenylmethane results in the formation of 3,3,3-triphenylpropionaldehyde, i.e. C-alkylation occurs, without transfer of reaction center.

3. The previously undescribed vinyl esters of trichloroacetic, phenylacetic, triphenylacetic, phthalimidoacetic, p-nitrobenzoic acids have been prepared.

4. The synthesis and ozonization of 4,4,4-triphenyl-1-butene have been described.

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Received March 15, 1954

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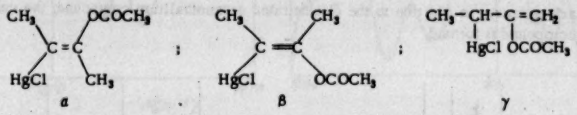
INVESTIGATION OF THE PRODUCTS OF THE ADDITION OF MERCURY SALTS TO DISUBSTITUTED ACETYLENES

A. E. Borisov, V. D. Vilchevskaya, and A. N. Nesmeyanov

In a previous paper we have described the addition of mercury salts to dimethyl- and diphenyl-acetylenes [1]. These reactions led to the preparation of new organomercury compounds of the ethylene series. Reaction of 2-butyne (dimethylacetylene) with mercuric acetate yielded three isomeric products, the α-, β-, and γ-isomers melting at 140°, 95°, and 130° respectively. The structures of these isomers were proved by ozonization, and it was shown that the α-, and β- compounds formed a pair of geometric isomers, and the γ-compound was structurally isomeric with these:



α ; β ; γ

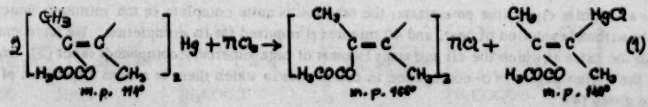
In the same paper we described some of the chemical and physical properties of these compounds.

We now describe a further investigation of the chemical and physical properties of these three compounds. A study of the infrared absorption spectra* has enabled us to determine the geometric configurations of the α- and β-isomers. The absorption spectrum of the α-isomer (Fig. 1) contains a frequency of 1667 cm^{-1} in the characteristic region of the C=C bond, whereas the spectrum of the β-isomer (Fig. 2) contains a frequency of 1655 cm^{-1} in the same region. The spectra contain also a frequency of 1755 cm^{-1} corresponding to the C=O group, which is present in both compounds.

Hence, a higher C=C frequency was found for the α-isomer than that found in the same region for the β-isomer. The more highly symmetrical trans compound generally has the higher C=C frequency [2], and for this reason we have ascribed the trans configuration to the α-isomer, and the cis configuration to the β-isomer. This assignment of configurations is in accord with the fact that the α-isomer is of lower solubility in organic solvents and has a higher melting point than the β-isomer - most trans compounds are related in this way to their cis isomers.

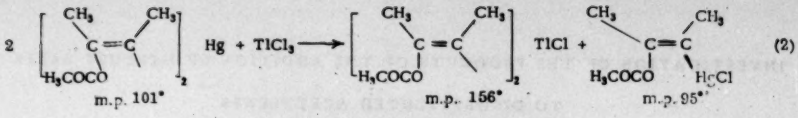
By the same method we have established the configurations of the symmetrical stereoisomers of bis(2-acetoxy-1-methylpropenyl)mercury. The stereoisomer prepared from the α-isomers had a C=C frequency of 1621 cm^{-1} (Fig. 3), whereas its stereoisomer, prepared from the β-isomer, had a C=C frequency of 1616 cm^{-1} (Fig. 4). On the basis of this difference in frequency we consider that the stereoisomer of bis(2-acetoxy-1-methylpropenyl)mercury of m.p. 114° has the trans-trans configuration, and the other isomer has the cis-cis configuration. The absence of a third stereoisomer having the cis-trans configuration was proved by the fact that the reaction of the trans-trans isomer with mecuric chloride yielded only pure trans-2-acetoxy-1-methylpropenylmercury chloride and the reaction of the cis-cis isomer with the same reagent yielded only cis-2-acetoxy-1-methylpropenylmercury chloride without any trans-isomer as by-product.

It has been shown previously [1] that the α-, β-, and γ-isomers are readily symmetrized to the corresponding fully substituted organomercury compounds. Each of these three symmetrical compounds (the cis-cis/trans-trans pair and their structural isomer) readily reacts with thallium trichloride in an ether medium, forming the corresponding disubstituted organothallium compound by the equation:

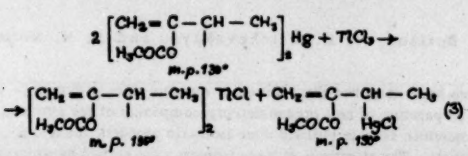


(1)

* At our request D. N. Shigorin determined the infrared absorption spectra, and we are very much indebted to him for this.



(2)



(3)

The organothallium compounds obtained by reactions (1), (2), and (3) are white crystalline substances melting respectively at 166°, 156°, amd 195°. They are soluble in alcohol, acetone, and hot water, but insoluble in benzene and ether. In each reaction, in addition to the disubstituted organothallium compound, the corresponding (α, β, or γ) organomercury compound is formed.

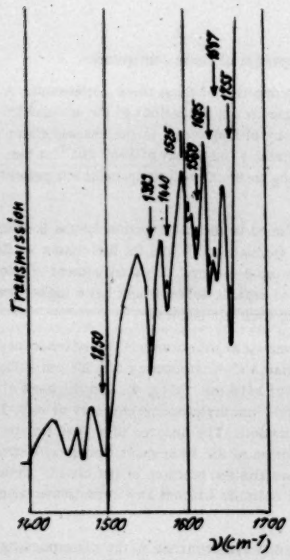


Fig. 1

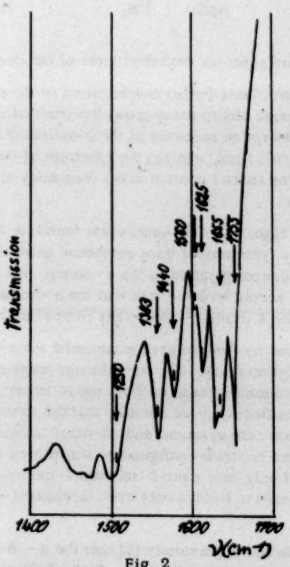
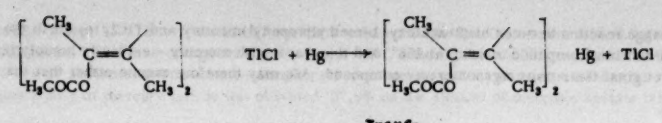


Fig. 2

The investigation of this reaction revealed that the stereoisomers of bis(2-acetoxy-1-methylpropenyl)mercury differed in their reactivities toward thallium trichloride: the trans-trans isomer is more reactive than the cis-cis isomer obtained from the β-compound. Reaction (1) proceeds instantaneously with evolution of heat, and the reaction product separates as a white crystalline precipitate; the reaction is quite complete in ten minutes. Reaction (2) proceeds more sluggishly without evolution of heat, and 40 minutes is required for its completion. We have thus again observed a difference in the rates at which the cis and trans isomers of organomercury compounds react [3]. We explain this difference by the higher degree of σ-conjugation in compounds in which there is a trans disposition of metal relative to an anionoid group [4].

The high-melting bis(2-acetoxy-1-methylpropenyl)thallium chloride reacts with mercury in acetone and yields the original trans-trans-bis(2-acetoxy-1-methylpropenyl)mercury, m.p. 114°.



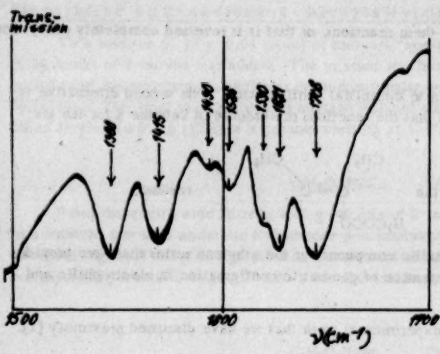


Fig. 3

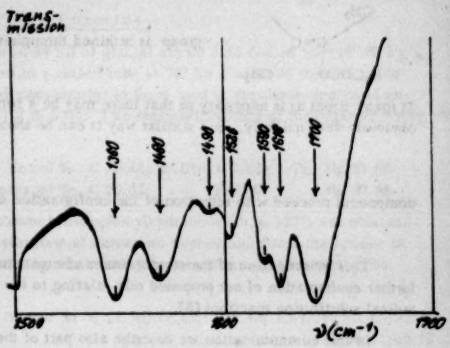
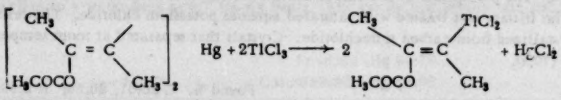


Fig. 4

The low-melting organothallium compound (m.p. 156°) reacts similarly with mercury, the sole product being cis-cis-bis(2-acetoxy-1-methylpropenyl)mercury (m.p. 101°).

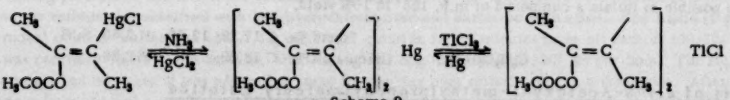
We now describe also the preparation of monosubstituted organothallium compounds of the type $RTlCl_2$ from disubstituted mercury compounds and $TlCl_3$. The reaction of trans-trans-bis(2-acetoxy-1-methylpropenyl)mercury with $TlCl_3$ in a molar ratio of 1 : 2 proceeds according to the equation:



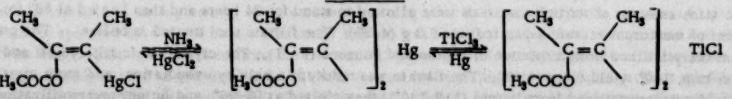
and yields a 2-acetoxy-1-methylpropenylthallium dichloride, a colorless crystalline substance, readily soluble in alcohol, acetone, and hot water, and insoluble in benzene and ether; it decomposes without melting at 141°. A second reaction product is mercuric chloride, which may be isolated as mercuric sulfide. Hence, in this reaction both organic residues pass from the mercury atom to the thallium atom; this behavior may be contrasted with that found in the preparation of R_2TlCl, in which the second product is an unsymmetrical organomercury compound. The cis-cis isomer reacts with $TlCl_3$ in a completely similar way and yields a 2-acetoxy-1-methylpropenylthallium dichloride that decomposes without melting at 135°. There is again a noteworthy difference in the rates of reaction, the reaction of the trans-trans isomer being the more rapid.

This investigation of geometric isomerism may be represented diagrammatically as follows:

Scheme 1

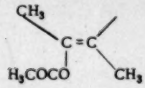


Scheme 2

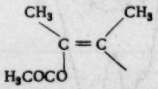


The configurations of the stereoisomers of 2-acetoxy-1-methylpropenylmercury chloride and of bis(2-acetoxy-1-methylpropenyl)mercury are known. Hence, the symmetrization reactions and the reverse reactions of dissymmetrization proceed with retention of the geometric configuration of the 2-acetoxy-1-methylpropenyl residue.

The exchange reaction between bis(2-acetoxy-1-methylpropenyl)mercury and $TlCl_3$ results in the formation of a pure organothallium compound melting at 166°, and this reacts with mercury - evidently homolytically - and yields the pure original trans-trans organomercury compound. We may therefore assume either that the configuration of the



-group is retained throughout these reactions, or that it is reversed completely every time - as many times as is necessary so that there may be a return to the initial configuration. The second alternative is obviously very unlikely. In a similar way it can be shown that the reactions represented in Scheme 2 for the cis compounds proceed with retention of the configuration of the



residue.

This investigation of the stereoisomers of organometallic compounds of the ethylene series therefore provides further confirmation of our proposed rule relating to the retention of geometric configuration in electrophilic and radical substitution reactions [5].

In this communication we describe also part of the experimental work that we have discussed previously [1].

EXPERIMENTAL

Synthesis of trans-2-Acetoxy-1-methylpropenylmercury Chloride

A solution of 7 g (0.02 mole) of mercuric acetate in 25 ml of glacial acetic acid was cooled to -18°, and 1.2 g (0.02 mole) of 2-butyne (b.p. 28°), previously cooled with a mixture of ice and salt, was added. The reaction mixture was allowed to stand in a sealed glass tube at room temperature. After 24 hours the tube was cooled with ice and salt and then opened. The precipitate of mercurous acetate was separated and dried (0.20 g, i.e. 3.5% of the theoretical amount). The filtrate was treated with saturated aqueous potassium chloride. The resulting precipitate was separated and recrystallized from carbon tetrachloride. Crystals that separated at room temperature melted at 140°; the yield was 5.4 g (70%).

	Found %:	C 20.61; 20.55;	H 2.59; 2.64;	Hg 57.74	
$C_6H_9O_2HgCl$.	Calculated %:	C 20.62;	H 2.59	Hg 57.46	

When the filtrate was cooled, 0.4 g (5%) of a substance of m.p. 95-96° separated. From the acetic acid filtrate 1 g (19%) of mercury sulfide was obtained.

It was found that treatment of the filtrate with saturated aqueous sodium bromide gave the corresponding bromide, m.p. 162-163°, in 65% yield.

	Found %:	C 18.48; 18.36;	H 2.32; 2.36;	Br 20.61; 20.46; Hg 50.86; 50.76
$C_6H_9O_2HgBr$.	Calculated %:	C 18.29;	H 2.28	Br 20.31; Hg 50.91

It was also possible to isolate a compound of m.p. 105° in 10% yield.

	Found %:	C 17.72; 17.60;	H 2.53; 2.31
$C_6H_9O_2HgBr$.	Calculated %:	C 18.29;	H 2.28

Synthesis of cis-2-Acetoxy-1-methylpropenylmercury Chloride

The same amounts of starting materials were allowed to stand for 24 hours and then heated at 56° for two hours. The amount of mercurous acetate separated was 0.3 g (4.5%). The filtrate was treated as before. The precipitate formed was recrystallized from a mixture of ligroin and benzene (2 : 1). The crystals were filtered off and recrystallized twice: m.p. 140°, yield 0.4 g (4.4%). The filtrate was reduced in bulk by evaporation, and more crystals (needles) separated. When recrystallized from ligroin (110-130°), they melted at 95-96°, and further recrystallizations did not affect the melting point. Yield 3.66 g (40.4%).

	Found %:	C 20.65; 20.83;	H 2.66; 2.73;	Hg 57.28
$C_6H_9O_2HgCl$.	Calculated %:	C 20.62;	H 2.59;	Hg 57.46

A fraction of b.p. 95-110° was distilled from the acetic acid solution. On reaction with 0.5 g of p-nitrophenylhydrazine this gave a crystalline orange substance of m.p. 125°, raised to 126-127° by recrystallization from alcohol. A mixture test with authentic 2-butanone p-nitrophenylhydrazone showed no depression. From the residue in the distilling flask 2.26 g of mercury sulfide was obtained (37.6% on the amount of mercuric acetate taken for reaction).

Preparation of 2-Acetoxy-1-methylallylmercury Chloride

To a solution of 13 g (0.04 mole) of mercuric acetate in 39 ml of glacial acetic acid cooled to −18°, 2.2 g (0.04 mole) of 2-butyne was added. The mixture was heated in a sealed tube at 76° for 2 hours 30 minutes. The isolation of the reaction products was carried out under conditions similar to those used in the above-described experiments. The amount of mercurous acetate isolated was 1 g (9.5 %). Two recrystallizations of the organomercury chloride yielded 2.4 g (17%) of a product melting at 130°.

		Found %:	C 20.44; 20.61;	H 2.63; 2.72;	Hg 57.30
$C_6H_9O_2HgCl$.		Calculated %:	C 20.62;	H 2.59;	Hg 57.46

From the acetic acid filtrate 3.45 g (40.5%) of 2-butanone p-nitrophenylhydrazone (m.p. 127°) was obtained. In a mixture test with authentic 2-butanone p-nitrophenylhydrazone it showed no depression. From the residue in the distilling flask 2.7 g of HgS (28% on the amount of mercuric acetate taken for reaction) was obtained. The corresponding bromide, m.p. 127-128°, was also isolated.

		Found %:	C 18.50; 18.69;	H 2.43; 2.54;	Br 20.41; 20.31; Hg 50.83; 50.79
$C_6H_9O_2HgBr$.		Calculated %:	C 18.29;	H 2.28;	Br 20.31; Hg 50.98

Ozonization of 2-Acetoxy-1-methylallylmercury Chloride

2-Acetoxy-1-methylallylmercury chloride (10 g; m.p. 130°) was ozonized in dry chloroform (40 ml) for six hours with ozonized oxygen (6% of ozone), which was passed at 4 liters per hour. The white crystalline precipitate that formed before the ozonide was decomposed with water gave the characteristic yellow of hydrated mercuric oxide. The decomposition was effected by addition of 50 ml of water to the ozonide, together with the precipitate, and heating of the mixture in a water bath at 60° for six hours. The crystalline precipitate was separated, washed, and dried.

	Found%:	Hg 84.79
Hg_2Cl_2.	Calculated%:	Hg 84.96

The filtrate was carefully neutralized with sodium carbonate. The chloroform layer was separated, and the aqueous layer was extracted with ether. The ether and chloroform extracts were united, dried with potassium carbonate, and transferred to a crystallizing dish; After the solvent had been evaporated off in the crystallizing dish, no reaction products could be detected. It was shown by the calomel method that formate was present in the aqueous solution of salts of organic acids. The greater part of this solution was evaporated to dryness on a water bath. A test by the cacodyl method on a small portion of the residue proved the presence of acetate. The remainder of the residue was treated with 10% hydrochloric acid solution, and the organic acids were extracted with ether. The extract was dried with sodium sulfate, and the ether was driven off. The residue was acidified with dilute sulfuric acid, and volatile acids (formic and acetic) were steam-distilled off, leaving behind any lactic acid that might be present.

The distillate was neutralized with sodium carbonate and heated with an aqueous solution of mercuric chloride. The glistening precipitate that formed — calomel — was filtered off, the solution was evaporated to dryness on a water bath, and the residue was acidified with 10% hydrochloric acid and extracted with ether. The liquid (1 g) remaining after removal of ether was heated with 1.1 g of thionyl chloride for 30 minutes in an oil bath at 100-120°. p-Toluidine (1.7 g) was carefully added to the mixture, and heating was continued at 120-130° for one hour. The liquid product obtained crystallized out when it was allowed to stand for one day over sulfuric acid in a dessicator. After two crystallizations from alcohol a product melting at 152° was obtained. A mixture test with p-acetotoluidide prepared by the same method showed no depression. The residue remaining after removal of volatile acids was filtered, and the solution was evaporated on a water bath. The sirupy residue was acidified with dilute sulfuric acid and repeatedly extracted with ether. Ether was distilled from the extract, 0.25 g of p-toluidine was added to the liquid residue (0.3 g), and the mixture was heated at 130-140° in an oil bath for two hours. The resulting liquid product solidified when cooled. Two recrystallizations from water yielded 0.05 g of the p-toluidide of lactic acid in the form of snow-white silky plates, m.p. 100.5-101.5°, undepressed by admixture of authentic p-toluidide of lactic acid (m.p. 101-102°).

Ozonization of cis-and trans-2-Acetoxy-1-methylpropenylmercury Chlorides

The ozonization of 7 g of 2-acetoxy-1-methylpropenylmercury chloride (m.p. 140°), the decomposition of

the ozonide, and the isolation of the reaction products were carried out under the conditions used in the preceding experiment. The chloroform and ether extracts contained no neutral products. No formate could be detected in the aqueous solution of salts of organic acids.

The aqueous solution was evaporated to dryness on a water bath. A small part of the dry residue was tested by the cacodyl test with arsenious oxide, and the presence of acetic acid was detected. Also, in order to confirm the presence of acetic acid, its p-toluidide, m.p. 152°, was obtained (no depression in a mixture test).

The ozonization of 2-acetoxy-1-methylpropenylmercury chloride (m.p. 95-96°), the decomposition of the ozonide, and the identification of the products was carried out as in the preceding experiments. Only acetic acid was detected in the products obtained by decomposing the ozonide. Acetic acid was proved by the cacodyl test and the preparation of its crystalline p-toluidide, m.p. 152°, undepressed by admixture of authentic p-acetotoluidide.

Reaction of Bis(2-acetoxy-1-methylpropenyl)mercury (M.p. 113°) with Thallium Trichloride

A solution of 0.18 g (0.0005 mole) of thallium trichloride in 5 ml of absolute ether was added at room temperature to a solution of 0.5 g (0.001 mole) of bis(2-acetoxy-1-methylpropenyl)mercury (m.p. 113°) in 10 ml of absolute ether. There was a slight rise in temperature, and a white crystalline precipitate was formed immediately. It was filtered off and washed three times with hot benzene. After recrystallization from aqueous alcohol it melted at 165-166° with decomposition. A further recrystallization did not affect the melting point. The yield was 0.26 g (96%). The substance was found to be soluble in acetone, alcohol, and hot water, and insoluble in ether, benzene, and petroleum ether.

The ether and benzene filtrates were evaporated under reduced pressure, and the dry residue was recrystallized twice from a mixture of petroleum ether (b.p. 90-110°) and benzene (2 : 1), when 0.38 g (95%) was obtained, m.p. 139-140°, undepressed by admixture of authentic 2-acetoxy-1-methylpropenylmercury chloride.

	Found %:	C 30.84; 30.94;	H 3.84; 3.75;	Cl 7.71; 7.69
$C_{12}H_{18}O_4TlCl$.	Calculated %:	C 30.84;	H 3.86;	Cl 7.62

Preparation of Bis(2-acetoxy-1-methylpropenyl)mercury Chloride having a Melting Point of 156°

A solution of 0.18 g (0.0005 mole) of thallium trichloride in 5 ml of absolute ether was added to a solution of 0.5 g (0.001 mole) of bis(2-acetoxy-1-methylpropenyl)mercury (m.p. 101-102°) in 30 ml of absolute ether. In this preparation the crystalline precipitate began to appear ten minutes after the ethereal solutions were mixed, and 40 minutes passed before the presence of thallium trichloride in the ethereal solution could no longer be detected.

The method of separating the reaction products was similar to that used in the preceding experiment. The precipitate, after being washed with benzene and recrystallized twice from alcohol, melted at 155-156° with decomposition. A further recrystallization did not affect the melting point. The yield was 0.26 g (96.7%).

	Found %:	C 30.77; 30.53;	H 3.96; 4.00;	Cl 7.97; 7.77
$C_{12}H_{18}O_4TlCl$.	Calculated %:	C 30.84;	H 3.86;	Cl 7.62

From the ether and benzene solutions 0.39 g (98%) of a substance of m.p. 90-95° was isolated. After recrystallization from petroleum ether it melted at 94-96°, undepressed by admixture of authentic 2-acetoxy-1-methylpropenylmercury of m.p. 95°.

Synthesis of Bis(2-acetoxy-1-methylallyl)thallium Chloride

Reaction between 0.5 g (0.001 mole) of bis(2-acetoxy-1-methylallyl)mercury (m.p. 130°) with 0.18 g (0.0005 mole) of thallium trichloride in 5 ml of absolute ether was carried out under conditions similar to those of the previous experiments. A crystalline precipitate was formed immediately. It was washed with benzene and recrystallized from aqueous alcohol. The yield was 0.25 g (92.6%). When the crystals were heated in a sealed capillary, they blackened at 195° and had still not melted at 300°. The product was soluble in acetone, alcohol, and hot water, but insoluble in ether, benzene, and petroleum ether.

	Found %:	C 30.95; 30.82;	H 4.12; 4.05;	Cl 7.54; 7.59
$C_{12}H_{18}O_4TlCl$.	Calculated %:	C 30.84;	H 3.86;	Cl 7.62

From the ether and benzene filtrates 0.4 g (98%) of a substance melting at 120-129° was isolated. After recrystallization from a mixture of petroleum ether and benzene (2: 1), it melted at 120-130°, and the melting point was not depressed by admixture of authentic 2-acetoxy-1-methylallylmercury chloride.

Reaction of Bis(2-acetoxy-1-methylpropenyl)thallium Chloride of Melting Point 166° with Mercury

Mercury (2.3 g) and a solution of 0.25 g of bis(2-acetoxy-1-methylpropenyl)thallium chloride of m.p. 166° in 40 ml of acetone were placed in a two-necked cylindrical flask fitted with stirrer and reflux condenser. The reaction mixture was stirred vigorously at 60° for ten hours. The solution was separated from thallous chloride and unchanged mercury, and then evaporated to dryness. The residue was extracted with benzene, and after removal of the benzene, crystals melting at 107-111° were obtained.

After two recrystallizations from petroleum ether (b.p. 40-60°) they melted at 112-113°. A mixture with authentic bis(2-acetoxy-1-methylpropenyl)mercury melted at 112.5-113°. The yield of recrystallized product was 0.09 g (40.9%).

Reaction of Bis(2-acetoxy-1-methylpropenyl)thallium Chloride of Melting Point 156° with Mercury

The reaction of 0.4 g of bis(acetoxy-1-methylpropenyl)thallium chloride of m.p. 156° with 3 g of mercury was carried out under conditions similar to those of the preceding experiment, and 0.18 g (50%) of a crystalline substance of m.p. 101° was isolated. There was no depression in a mixture test with previously synthesized bis(2-acetoxy-1-methylpropenyl)mercury.

Synthesis of 2-Acetoxy-1-methylpropenylthallium Dichloride having a Decomposition Temperature of 141°

When ethereal solutions of 0.5 g (0.001 mole) of bis(2-acetoxy-1-methylpropenyl)mercury of m.p. 113° and of 0.72 g (0.002 mole) of thallium trichloride were mixed, there was an immediate white crystalline precipitate, which was filtered off after ten minutes, washed repeatedly with ether, and then recrystallized from water. When heated in a sealed capillary, the dried product blackened at 141° without melting; neither did it melt when recrystallized from aqueous alcohol or from water. The product was 0.85 g (93%) of 2-acetoxy-1-methylpropenylthallium dichloride. The substance is soluble in acetone, alcohol, and hot water, but insoluble in ether and benzene.

	Found %:	C 18.65; 18.56;	H 2.44; 2.47;	Cl 17.59; 17.57
$C_6H_9O_2TlCl_2$.	Calculated %:	C 18.53;	H 2.35;	Cl 18.28

The solvent was distilled from the filtrate obtained after separation of the 2-acetoxy-1-methylpropenylthallium dichloride, and the dry residue was dissolved in cold water. The solution was acidified with dilute hydrochloric acid and treated with hydrogen sulfide. The resulting precipitate of mercuric sulfide (Tl_2S is not precipitated by hydrogen sulfide from acidified aqueous solution) was filtered off through a Gooch crucible and carefully washed with cold concentrated sulfuric acid to remove any possible Tl_2S impurity. The precipitate was washed with water, with alcohol, and with ether, and dried at 110° to constant weight. The yield of HgS was 0.24 g, corresponding to 0.28 g of mercuric chloride (90% of the theoretical amount).

Preparation of 2-Acetoxy-1-methylpropenylthallium Dichloride having a Decomposition Temperature of 135°

An ethereal solution of 2.16 g (0.006 mole) of thallium trichloride was added at room temperature to an ethereal solution of 1.5 g (0.003 mole) of bis(2-acetoxy-1-methylpropenyl)mercury of m.p. 101°. Separation of the crystalline precipitate did not begin until ten minutes had passed. After the mixture had stood for 40 minutes at room temperature, the precipitate was separated, washed with ether, and recrystallized from water. The yield of product was 80%. It decomposed at 135°, and after recrystallization from alcohol it still decomposed, without melting, at 135°. The substance readily dissolves when heated with alcohol, acetone, or water, but is of poor solubility in benzene and ether.

	Found %:	C 18.72; 18.85;	H 2.48; 2.55;	Cl 18.20; 18.05
$C_6H_9O_2TlCl_2$.	Calculated %:	C 18.53;	H 2.35;	Cl 18.28

Mercuric chloride was separated as in the previous experiment; 0.78 g of HgS was obtained, which corresponds to 0.9 g (94%) of $HgCl_2$.

SUMMARY

1. On the basis of a study of their infrared absorption spectra, the *a*-isomer of 2-acetoxy-1-methylpropenylmercury chloride, which has a C=C frequency at 1667 cm^{-1}, is assigned the trans configuration, and its stereoisomer, which has a C=C frequency of 1655 cm^{-1}, is assigned the cis configuration.

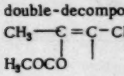
2. Bis(2-acetoxy-1-methylpropenyl)mercury of m.p. 114°, which has a C=C frequency of 1621 cm^{-1}, has been assigned to the trans series, and its stereoisomer of m.p. 101°, which is obtained from the β-compound and has a C=C frequency of 1616 cm^{-1}, has been assigned the cis-cis configuration.

3. Two new stereoisomeric bis(2-acetoxy-1-methylpropenyl)thallium chlorides have been synthesized from the stereoisomeric bis(2-acetoxy-1-methylpropenyl)mercurys and thallium trichloride, and some of their chemical properties have been investigated. Their geometric configurations have been established by the method of even and odd cycles.

4. It has been shown that the stereoisomeric bis(2-acetoxy-1-methylpropenyl)mercurys react at different rates with thallium trichloride, the trans-trans compound reacting much more rapidly than the cis-cis isomer.

5. A new reaction has been described in which organothallium compounds of the type $RTlCl_2$ are synthesized directly from symmetrical organomercury compounds and thallium trichloride.

6. By means of a symmetrization reaction, bis(2-acetoxy-1-methylallyl)mercury has been prepared, and some of its chemical properties have been studied. It reacts with thallium trichloride with formation of bis(2-acetoxy-1-methylallyl)thallium chloride.

7. It has been shown that in the symmetrization and reverse dissymmetrization reactions, and also in the double-decomposition reactions with metal salts, the transfers of the 2-acetoxy-1-methylpropenyl group  from one metal atom to another and back occur without any change in geometric configuration. This behavior confirms the rule that we have established relating to the preservation of the configurations of cis and trans isomers in metathetic reactions with electrophilic reagents and in homolytic exchange reactions.

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Received February 13, 1954

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DECOMPOSITION AND FORMATION OF ONIUM SALTS AND THE SYNTHESIS OF HETERO-ORGANIC COMPOUNDS

COMMUNICATION 8. DECOMPOSITION OF BENZENEDIAZONIUM FLUOBORATE IN PRESENCE OF NITRILES

L. G. Makarova and A. N. Nesmeyanov

We have shown in previous investigations [1, 2] that benzenediazonium and diphenyliodonium fluoborates decompose heterolytically. The heterolytic character of the decomposition of benzenediazonium fluoborate was proved by observations on the orientation of entering groups both in substitution reactions with benzene derivatives (the phenyl cation formed by the decomposition of benzenediazonium fluoborate was found to enter the meta position with respect to an orienting group of the second kind), and also in addition reactions with unsaturated compounds. In the present investigation we have studied the decomposition of benzenediazonium fluoborate in presence of nitriles.

It was thought that the phenyl cation formed by the decomposition of benzenediazonium fluoborate would add at the point of highest electron density in the nitrile molecule – the nitrogen of the nitrile group – with the formation of anilides, in accordance with the scheme:

$$RC\equiv N + C_6H_5^+ + F^- \longrightarrow RCF=NC_6H_5 \xrightarrow{H_2O} RC(OH)=NC_6H_5 \rightleftharpoons RC(=O)-NHC_6H_5$$

Also, it could be expected that, as a result of the decomposition of benzenediazonium fluoborate in a medium of benzonitrile (or other aromatic nitrile), 3-biphenylcarbonitrile (or one of its homologs) would be formed by entry of the phenyl cation into the benzene nucleus in the meta position to the meta-orienting nitrile group.

On the other hand, the possibility could not be excluded that the diazonium form would be converted into the diazo form under the influence of the free pair of electrons on the nitrogen of the nitrile group, which is what actually occurs when benzenediazonium fluoborate decomposes in pyridine, in presence of hydroxyl ions, or in presence of metals:

$$C_6H_5N\equiv N: + :\ddot{O}H \longrightarrow C_6H_5\overset{\oplus}{N}=\overset{\ominus}{N}: \longrightarrow C_6H_5\bar{N}=\bar{N}-$$

The decomposition of the diazo form, however, would be homolytic, with forma ion of an aryl radical; and by reaction of this aryl radical with the nitrile, not only the anilide, but also other products would be formed, in particular ketones and, when aromatic nitriles are used, also derivatives of 2- or 4-biphenylcarbonitrile. The phenyl radical formed by the decomposition of benzenediazohydroxide enters the benzene nucleus in the para position to the nitrile group with formation of 4-biphenylcarbonitrile [3].

Hanby and Waters [4] found that, in the decomposition of benzenediazonium chloride in acetonitrile, a mixture of substances was formed – benzene, chlorobenzene, and about 10% of acetanilide – and this was interpreted by them as proof of the homolytic character of the decomposition of arenediazonium chlorides. When the decomposition was carried out in propionitrile, Hanby and Waters found only benzene and chlorobenzene in the products and could not detect any propionanilide. They were unable to identify any reaction products in the decomposition of benzenediazonium chloride in a medium of phenylacetonitrile.

In the decomposition of arenediazonium chlorides in aqueous acetone solution in presence of acrylonitrile, sodium acetate, and a cupric salt, Koelsch [5] obtained 30-40% yields of products of the addition of aryl at the double bond, namely, nitriles of α-chlorohydrocinnamic acids. This must be considered to prove that the decomposition of the diazo compounds investigated by Koelsch is homolytic and is followed by addition of an aryl radical at a double bond. Koelsch did not observe addition of aryl to the nitrogen of acrylonitrile.

We have carried out the decomposition of benzenediazonium fluoborate in the following media: benzonitrile, p-tolunitrile, o-tolunitrile, phenylacetonitrile, acetonitrile, propionitrile, and acrylonitrile. It was found that phenyl added at the nitrogen of the nitrile group with formationof the corresponding anilides, the yields being 40 % from benzonitrile, p-tolunitrile, and phenylacetonitrile, 30 % from o-tolunitrile and acetonitrile, 15 % from propionitrile, and 10 % from acrylonitrile. No ketone formation was observed in any of these reactions. In the reactions with aromatic nitriles, phenyl did not enter the aromatic nucleus – no biphenyl derivatives were formed. Also, when the decomposition occurred in a medium of acrylonitrile, no identifiable products arising by the addition of phenyl at the carbon-carbon double bond were obtained. Formation of anilides was accompanied by the polymerization of the nitriles, evidently resulting from the promoting action of boron trifluoride, and in the reactions with benzonitrile and p-tolunitrile the trimers were isolated; in the other reactions the occurrence of polymerization was shown by the formation of high-boiling substances or undistillable (acrylonitrile) resins.

The following facts, therefore, indicate that the mechanism of the reaction that we have investigated is different from that of the reactions of Hanby and Waters, Koelsch, and Gomberg and Bachmann, and that it consists, in fact, of the action of a phenyl cation, formed by the heterolytic decomposition of benzenediazonium fluoborate, on the nitrile: first, the greatly increased yields of anilides in the decomposition of benzenediazonium fluoborate in nitrile media, as compared with the yields obtained by Hanby and Waters in the decomposition of benzenediazonium chloride (for acetonitrile 10 to 30 %, for phenylacetonitrile 0 to 40 %, and for propionitrile 0 to 14 %); second, the absence of ketone formation by the action of radicals on the nitriles; and finally, the formation of essentially different products (comparison of the decomposition of benzenediazonium fluoborate in acrylonitrile and benzonitrile media with the decomposition of arenediazonium chloride in acrylonitrile and benzenediazohydroxide in benzonitrile).

EXPERIMENTAL

Decomposition of Benzenediazonium Fluoborate in a Benzonitrile Medium

The decomposition was carried out in a four-necked cylindrical flask placed in an oil bath and fitted with mercury-sealed stirrer, reflux condenser, and thermometer. The fourth opening of the flask was used for the addition of the diazonium salt. Benzenediazonium fluoborate was freshly prepared and dried in a desiccator over calcium chloride; 150 g (one molecular proportion) of it was added in small portions over a period of 80 minutes to 225 g (2.8 molecular proportions) of benzonitrile at 70°. The reaction was exothermic, and after addition of the first portion of diazonium salt the temperature rose to 80°. Further additions were therefore made without external heating, the rate of addition being adjusted so that the temperature did not rise above 80°. The reaction mixture gradually darkened, white fumes were evolved, and deliquescent crystals containing boron trifluoride, formed in the condenser. When the addition of the diazonium salt was complete, the mixture was heated at 75° for 45 minutes. On the next day the mixture was dissolved in ether, the small amount of boron-containing inorganic precipitate being removed. When washed with 10% NaOH (500 ml), the ether solution yielded a voluminous precipitate, which was filtered off. From this precipitate, boiling ethanol extracted 33.4 g of benzanilide. After recrystallization from alcohol its melting point and the melting point of a mixture with known benzanilide were 163°. The alcohol-insoluble residue was crystallized from benzene and chloroform, and then melted at 232°. For kyaphenin (2,4,6-triphenyl-s-triazine) $(C_6H_5CN)_3$ Scholl and Norr [6] give m.p. 231-232°.

The ether solution was washed with water and dried with sodium sulfate. The residue remaining after removal of ether was vacuum-distilled.

Fraction I, b.p. 74- 76° (12 mm); 98 g
Fraction II, b.p. 120-167° (5 mm); 1 g
Fraction III, b.p. 185-205° (5 mm); 30 g
Fraction IV, b.p. 205-255° (5 mm); 13 g

Fraction I was benzonitrile; Fraction III solidified completely; Fraction IV was a viscous red oil, which partially solidified on standing. The crystals that formed from Fraction IV were separated from the oil and added to Fraction III. The mixture was crystallized from alcohol, acetone, or benzene, and the melting point of the product, and also of its mixture with known benzanilide, was 163°. The total yield of benzanilide was 61 g (39 %).

Found % C 78.94; 79.14; H 5.66; 5.52
$C_{13}H_{11}ON$. Calculated % C 79.16; H 5.61

Solvent was distilled from the mother liquor remaining from the crystallization of benzanilide, and the

residue was boiled with concentrated hydrochloric acid for three days. The hydrochloric acid solution was steam-distilled. Part of the distillate was extracted with ether, and the residue remaining after removal of ether from the extract was sublimed. The melting points of the product and of a mixture of it with benzoic acid were 121°. The remainder of the distillate was rendered alkaline and again steam-distilled; the new distillate was extracted with ether, and the ether extract was dried. After removal of ether a very small greasy residue remained, and this gave no precipitate with 2,4-dinitrophenylhydrazine.

Decomposition in a p-Tolunitrile Medium

Over a period of 75 minutes, 137 g (one molecular proportion) of benzenediazonium fluoborate was added in small portions to 143 g (1.7 molecular proportions) of p-tolunitrile heated to 70° in an oil bath. Reaction was exothermic, and the decomposition was carried out at 75-76° without external heating. When the addition of the diazonium salt was complete, the mixture was stirred for one hour in an oil bath at 70-75°. On the next day, the whole of the thick dark-colored mass was dissolved in ether, and the resulting solution was washed with 10% NaOH. A precipitate was then formed, and this, together with the ether layer, was washed with water. The ether was distilled off, and p-tolunitrile was vacuum-distilled from the residue. The semisolid substance that remained was vacuum-distilled, and boiled over the range 188-248°. The residue crystallized completely during the distillation. In its recrystallization from ethanol 5.7 g of alcohol-insoluble residue was obtained, and this, after crystallization from benzene and chloroform, melted at 280-281° (Francis and Davis [7] give m.p. 278° for 2,4,6-tri-p-tolyl-s-triazine).

	Found %	C 81.98; 82.38; H 5.99; 6.02
$C_{24}H_{21}N_3$.	Calculated %	C 82.05; H 5.98

The ethanol solution yielded 57.8 g of a substance melting at 142°, alone and in admixture with known p-toluanilide. The yield was 40.5%.

Decomposition in an o-Tolunitrile Medium

Over a period of 90 minutes, 120 g (one molecular proportion) of benzenediazonium fluoborate was added to 125 g (1.7 molecular proportions) of o-tolunitrile heated to 70°. The temperature was maintained at 70-72° by the heat of reaction. When the whole of the benzenediazonium fluoborate had been added, the mixture was stirred at the same temperature for 90 minutes. On the next day the dark-colored reaction mass was dissolved in ether, and the solution was washed with 10% NaOH and water. Ether and water were distilled off, and the residue was vacuum-distilled.

Fraction I,	b.p. 65- 74° (5 mm)
Fraction II,	b.p. 200-220° (5 mm); 31.14 g
Fraction III,	b.p. 212-268° (5 mm); 12.3 g

Fraction I was o-tolunitrile; Fraction II solidified; Fraction III came over toward the end as a noncrystallizing oil. Fractions II and III were combined and crystallized from ethanol, and 40 g (30.3 % was obtained of a substance melting at 125° (reported melting point of o-toluanilide, 125° [8]).

Decomposition in a Phenylacetonitrile Medium

Over a period of 75 minutes, 120 g (one molecular proportion) of benzenediazonium fluoborate was added to 200 g (2.7 molecular proportions) of phenylacetonitrile heated to 70°. The decomposition was carried out at 68-72° without external heating. When the whole of the diazonium salt had been added, the mixture was heated for one hour at 70°. On the next day the dark-colored oil was dissolved in ether — there was a small amount of ether-insoluble orange-red resinous residue. The ether solution was washed with 10% NaOH solution and with water; it was then dried with sodium sulfate. Ether was distilled off, and o-tolunitrile was removed under reduced pressure (b.p. 105-109° at 12 mm). Vacuum fractionation of the residue yielded Fraction I (200-240°/5 mm), 42 g and Fraction II (242-295°/5 mm), 16.3 g.

Fraction I solidified completely. Fraction II was a dark-red oil that partially solidified, and crystals were separated from the oil and added to Fraction I. Recrystallization of this mixture from ethanol yielded 49 g (39%) of a substance melting at 116° after recrystallization from benzene (the reported melting point of 2-phenylacetanilide is 116° [9]).

A test for ketone, carried out as in the experiment on benzonitrile, was negative.

Decomposition of an Acetonitrile Medium

Over a period of 30 minutes, 96 g (one molecular proportion) of benzenediazonium fluoborate was added to 151 g (7.3 molecular proportions) of acetonitrile heated to 72°. Decomposition occurred with vigorous foaming and slight fuming, and the temperature was maintained at 72° without external application of heat. When the whole of the benzenediazonium fluoborate had been added, the stirred mixture was heated at 72-76° for one hour. It was then dissolved in ether, and the ether solution was washed with 10% NaOH and with water; it was then dried with sodium sulfate. After removal of ether and excess of acetonitrile by distillation 27 g of an oil remained; it solidified when cooled. Vacuum distillation yielded:

Fraction I. b.p. 150-175° (7 mm); 20 g
Fraction II. b.p. 240-265° (7 mm); 1.82 g

A small amount of black resin remained in the flask. Fraction I solidified completely and, when crystallized from water, it yielded 16.3 g of white leaves melting, alone and in admixture with acetanilide, at 114°. Fraction II was a red, viscous mass, from which a little acetanilide separated on standing.

The alkaline wash liquors were acidified and extracted with ether, when a further 3.35 g of acetanilide m.p. 114, was obtained. The total yield of acetanilide was 19.7 g (29%). Fraction II and the mother liquors from the crystallization of acetanilide were tested for the presence of ketone as in the experiment on benzonitrile. No precipitate was formed with 2,4-dinitrophenylhydrazine.

Decomposition in a Propionitrile Medium

One molecular proportion (43 g) of benzenediazonium fluoborate was added in small portions to 35 g (three molecular proportions) of propionitrile heated to 68°. Addition of the first portion of the diazonium salt caused the temperature to rise to 78°; further additions were made at 70-75°. When the whole of the diazonium salt had been added, the mixture was stirred for one hour at 75°. On the next day the mixture was dissolved in ether. The ether solution was washed with 10% NaOH and with water, and was dried with sodium sulfate. Ether was distilled off, and the excess of propionitrile was distilled off under reduced pressure.

Fraction I. b.p. 65- 90° (6 mm); 0.83 g
Fraction II. b.p. 90-150° (6 mm); a few drops
Fraction III. b.p. 150-155° (6 mm); 5.64 g

Fraction III solidified completely. After being crystallized from benzene it melted at 105° (the reported melting point of propionanilide is 105° [10]). The yield was 5.08 g (15%).

Decomposition in an Acrylonitrile Medium

Over a period of one hour, 73 g (one molecular proportion) of benzenediazonium fluoborate was added in small portions to 80 g (four molecular proportions) of acrylonitrile heated to 70°. Toward the end of this time a precipitate of resin formed and the mixture foamed strongly. After addition was complete the mixture was stirred at the same temperature for 15 minutes. The reaction mixture consisted of an oil and a lump of red resin. The oil was extracted with ether and the resin was washed with ether, and the combined ether solutions were washed with 10% NaOH and with water, and were then dried with sodium sulfate. After removal of ether, there remained an oil, which slowly crystallized. The oil was distilled from a pear-shaped flask, and yielded 5.9 g (10.7 %) of an oil, b.p. 145-150° at 3 mm, which rapidly solidified. After being crystallized from acetone it melted at 105°, (the reported melting point of acrylanilide is 104-105° [1]). The residue in the flask was a dark-brown resin.

SUMMARY

1. By the decomposition of benzenediazonium fluoborate in a nitrile medium (benzonitrile, p- and o-tolunitriles, phenylacetonitrile, acetonitrile, propionitrile, and acrylonitrile), the corresponding anilides have been obtained in yields of up to 40%.

2. The occurrence of this reaction provides confirmation of the heterolytic character of the decomposition of benzenediazonium fluoborate.

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Received February 16, 1954

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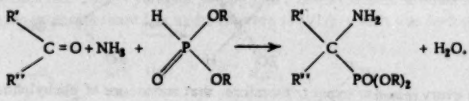
NEW METHOD FOR THE SYNTHESIS OF 1-AMINOALKYL-PHOSPHONIC AND -PHOSPHINIC ACIDS

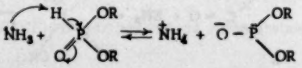
COMMUNICATION 4. SYNTHESIS OF (1-AMINOALKYL)PHENYLPHOSPHINIC ACIDS

M. I. Kabachnik and T. Ya. Medved

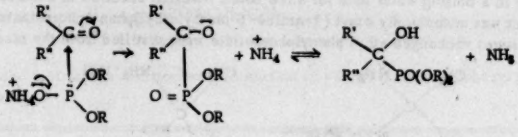
In previous communications [1] we have shown that a dialkyl hydrogen phosphite, an aldehyde or ketone, and ammonia will react together and yield a 1-aminoalkylphosphonic ester:



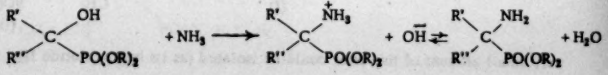
We treated the mechanism of this reaction as follows. We considered that the dialkyl phosphite ionizes in presence of ammonia, with transfer of reaction center and formation of a phosphite anion containing tervalent phosphorus:



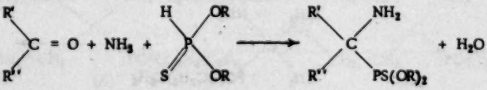
and this then adds to the carbonyl compound:



after which hydroxyl is replaced by amino:



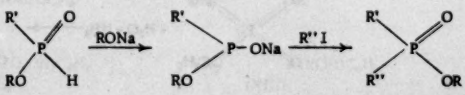
We then suggested that reactions of this type should be possible for the ammonium salts of all acids capable of diad or triad tautomerism [2]. For example, dialkyl phosphorothioites are acids of this type [3]. For this reason, these substances, as we have shown in our laboratory [4], react with carbonyl compounds and ammonia with formation of the corresponding esters of 1-aminoalkylphosphonothionic acids:



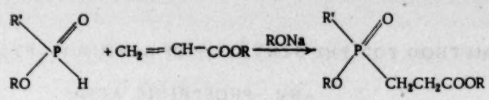
Monoesters of aryl (or alkyl)phosphonous acids are of the same type:

$$R-POH(OR) \text{ or } C_6H_5-POH(OR).$$

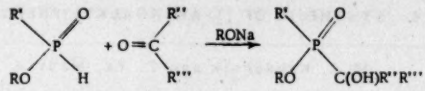
These substances are able to form metal derivatives, which react with alkyl halides by a reaction of the Michaelis-Becker type [5]:



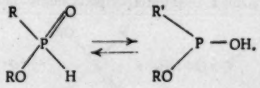
In presence of alkaline catalysts they add to an activated double bond, for example that of an acrylic ester [6]:



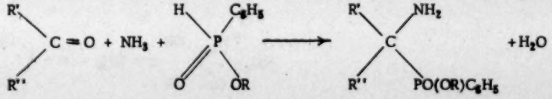
and they add also to carbonyl compounds with formation of alkyl(1-hydroxyalkyl)phosphinic esters:



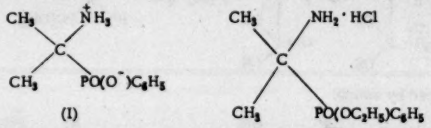
and they show all the other properties of diad-tautomeric substances:



There was every reason to expect, therefore, that monoesters of phenylphosphonous acid would react with carbonyl compounds in presence of ammonia with formation of the corresponding esters of (1-aminoalkyl)phenylphosphinic acids:



It was in fact found that, when a mixture of acetone, ethyl hydrogen phenylphosphonite, and alcoholic ammonia was heated in a sealed tube in a boiling water bath for three hours, reaction occurred in accordance with the foregoing scheme, and the product was undoubtedly ethyl (1-amino-1-methylethyl)phenylphosphinate. If, however, alcohol and (under reduced pressure) unchanged ethyl phenylphosphinite were distilled from the reaction mixture, only a

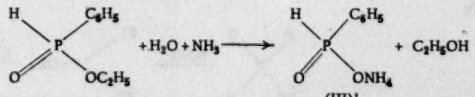


very small amount of this ester could be isolated (as its hydrochloride II). The main product isolated was the acid (I) (internal salt).

The same free acid is obtained when butyl phenylphosphonite is used instead of the ethyl ester. Reduction in the duration of heating results in only a slight increase in the yield of ester. It may be supposed that the ester formed in the reaction is decomposed by heat:

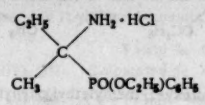
The low yield of ester may be explained also by partial hydrolysis of the original phosphonous ester.

It is in fact found that the ammonium salt of free phenylphosphonous acid (III) can always be found in the reaction products; it is formed by the hydrolysis of the original ester:

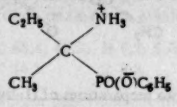


When the reaction between acetone, ethyl hydrogen phosphonite, and alcoholic ammonia is carried out at 150°, instead of 100°, this ammonium hydrogen phosphonite (III) is the main product.

In the reaction with 2-butanone, carried out in a boiling water bath for six hours, the main reaction product was ethyl (1-amino-1-methylpropyl)phenylphosphinate, isolated as its hydrochloride (IV):



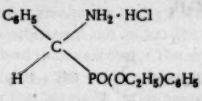
(IV)



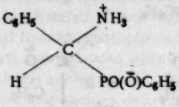
(V)

but when the duration of heating was 12 hours, only the free acid (V) could be isolated. The same acid was obtained by the hydrolysis of (IV).

The reaction between benzaldehyde, ethyl hydrogen phosphinate, and alcoholic ammonia resulted in the formation of ethyl (α-aminobenzyl)phenylphosphinate [its hydrochloride is (VI)], which was hydrolyzed to the free acid (VII):

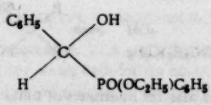


(VI)



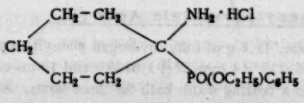
(VII)

Under milder conditions the hydroxy derivative (VIII) is obtained instead of the amino compound:



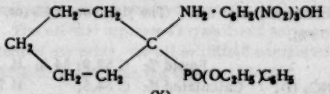
(VIII)

Cyclohexanone will also take part in this reaction with formation of ethyl(1-aminocyclohexyl)phenylphosphinate [the hydrochloride is (IX)]:

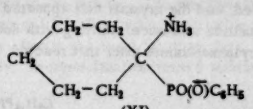


(IX)

The hydrochloride was converted into the free ester by treatment with sodium carbonate, and the ester was converted into its picrate (X). Hydrolysis of the hydrochloride (IX) with hydrochloric acid at 115-125° (sealed tube) yielded free (1-aminocyclohexyl)phenylphosphinic acid (XI):

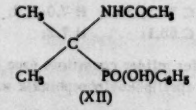


(X)

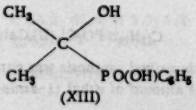


(XI)

In proving the structure of the amino phosphinic acids, we took (1-amino-1-methylethyl)phenylphosphinic acid as our working example. The presence of a free amino group was proved by acetylation of the acid to (1-acetamido-1-methylethyl)phenylphosphinic acid (XII) and by treatment with nitrous acid, which yielded the corresponding hydroxy acid (XIII):

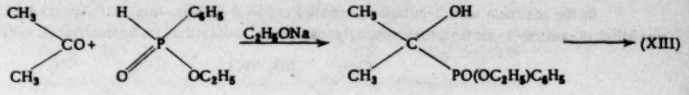


(XII)



(XIII)

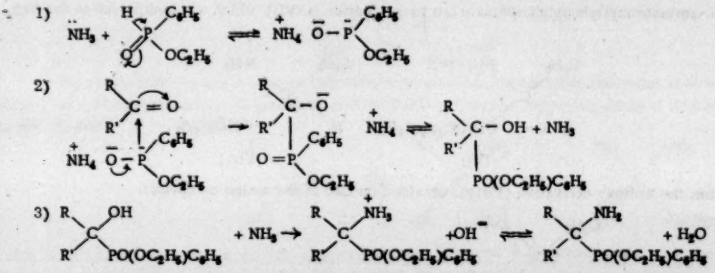
We synthesized the same acid, following Abramov [7], by addition of ethyl hydrogen phenylphosphonite to acetone and hydrolysis of the resulting ester (XIV):



(XIV)

The melting points of the two preparations of (1-hydroxy-1-methylethyl)phenylphosphinic acid were the same; there was no melting point depression when they were mixed.

We consider that the mechanism of the reaction described in the present paper is similar to that proposed by us for the reaction between a dialkyl phosphite, a carbonyl compound, and ammonia. We give it here without explanation:



We consider that similar reactions can occur also for monoesters of other alkyl- and aryl-phosphonous acids.

EXPERIMENTAL

(1-Amino-1-methylethyl)phenylphosphinic Acid (I)

a) A mixture of 4 g of acetone, 11.5 g of ethyl hydrogen phenylphosphonite (prepared from phenylphosphonous dichloride and ethanol [5, 6]; b.p. 116-117°/4 mm; n_D^{20} 1.5223), and 15 ml of a 10% solution of ammonia in absolute ethanol was heated in a sealed tube in a boiling water bath for three hours. Alcohol and excess of ammonia were removed under reduced pressure, the mixture being heated in a boiling water bath. The residue was fractionated, and 8 g of a clear colorless liquid came over at 115-117° and 4 mm; it was found to be unchanged ethyl hydrogen phenylphosphonite containing some substance of alkaline reaction as impurity. The residue in the flask became very thick, and it partially crystallized; it was dissolved in a small amount (2-3 ml) of boiling absolute ethanol. The solution was cooled, and the crystals that appeared were filtered off. Recrystallization from alcohol yielded 3.2 g of a colorless crystalline substance, melting with decomposition at 244°. The yield was 24% (or, calculated on the amount of the phenylphosphonous ester that reacted, 79%).

	Found %:	C 53.9;	54.3;	H 6.7;	6.7;	P 15.6;	15.5;	N 7.2;	7.3
$C_9H_{14}PNO_2$ (I).	Calculated %:	C 54.3;		H 7.0;		P 15.6;		N 7.0	

An aqueous solution of (1-amino-1-methylethyl)phenylphosphinic acid is neutral to litmus.

The distillate obtained from the reaction product was dissolved in dry ether, and dry hydrogen chloride was passed through the solution. The crystals that were precipitated (0.3 g) were reprecipitated from an alcohol-ether mixture, and then melted with decomposition at 166°.

	Found %:	C 50.3;	50.6;	H 7.0;	7.2;	P 12.1;	12.1;	N 5.5;	5.4
$C_{11}H_{19}NPO_2Cl$ (II).	Calculated %:	C 50.1;		H 7.2;		P 11.8;		N 5.3	

When the above-described synthesis was carried out under milder conditions (one hour at 100° or 20-25 days at 20°), a somewhat greater amount of ethyl (1-amino-1-methylethyl)phenylphosphinate was obtained, but the total yield was not increased.

Under more severe conditions (nine hours at 100° or three hours at 150°) no ethyl (1-amino-1-methylethyl)phenylphosphinate was obtained; the only product was ammonium hydrogen phenylphosphonite (III). In these experiments, after removal of alcohol and excess of ammonia from the reaction mixture, 2 ml of absolute ethanol was added to the residue, and this was followed by the addition of ether. The precipitate that then formed was filtered off. Reprecipitation from a mixture of alcohol and ether yielded 0.9 g of a colorless substance melting at 175°. It was readily soluble in water, and it yielded ammonia when treated with alkali.

		Found %:	C 45.4; 45.2;		H 6.2; 6.5;		P 19.6; 19.5;		N 8.1; 8.1
$C_6H_{16}NPO_2$ (III).	Calculated %:	C 45.3		H 6.3		P 19.5		N 8.8	

b) When a mixture of 4 g of acetone, 13.2 g of butyl hydrogen phenylphosphonite (b.p. 120-121° at 4 mm; n_D^{20} 1.5077) and 15 ml of a 10% solution of ammonia in ethanol was heated in a sealed tube in a boiling water bath for three hours, the same amount of (1-amino-1-methylethyl)phenylphosphinic acid was obtained as in the experiment described above.

(1-Amino-1-methylpropyl)phenylphosphinic Acid (V)

a) A mixture of 4.8 g of 2-butanone, 11.5 g of ethyl hydrogen phenylphosphonite, and 20 ml of a 10% solution of ammonia in absolute ethanol was heated in a sealed tube in a boiling water bath for 12 hours. On cooling, the solution yielded a colorless crystalline precipitate (0.2 g), which was filtered off and found to be ammonium hydrogen phenylphosphonite (III). Volatile substances and unchanged ethyl hydrogen phenylphosphonite (5 g) were then distilled off, and the residue was dissolved in hot alcohol. The crystals that appeared when the solution cooled were filtered off and recrystallized from alcohol. The product formed colorless crystals (yield 17%, or 30% calculated on the amount of phenylphosphonous ester that reacted). After being dried in a vacuum desiccator over phosphoric oxide, the substance melted with decomposition at 197-198°. It was very hygroscopic, and was neutral to litmus.

		Found %:	N 6.5; 6.4;		P 14.4; 14.5		
$C_{10}H_{16}NPO_2$ (V).	Calculated %:	N 6.6;		P 14.6			

b) A mixture of 4.8 g of 2-butanone, 11.5 g of ethyl hydrogen phenylphosphonite, and 20 ml of 10% alcoholic ammonia was heated in a boiling water bath for six hours. Alcohol and ammonia were then removed under reduced pressure, and ether was added to the residue. The precipitate formed was filtered off (1.5 g of ammonium hydrogen phenylphosphonite), and dry hydrogen chloride was passed through the solution. An oil was thrown out, and this finally solidified after standing for three days and being rubbed in presence of dry ether. The substance was reprecipitated from an alcohol-ether mixture. The product was 8 g of (IV), m.p. 156-157°. It was difficult to purify (from ammonium chloride and the hydrochloride of the acid) and the analytical results were somewhat low.

The hydrochloride (IV) was hydrolyzed with hydrochloric acid in sealed tubes (three hours at 120-130°). The solution was evaporated on a water bath, and in order to remove hydrochloric acid from the residue, the latter was again dissolved in water, accuratedly neutralized, and evaporated to dryness. The dry residue was extracted with hot ethanol. Crystallization from alcohol yielded a substance melting at 197-198° (yield about 30%).

Hydrochloride of Ethyl (α-Aminobenzyl)phenylphosphinic Acid (VI)

A mixture of 7 g of benzaldehyde, 11.5 g of ethyl hydrogen phenylphosphonite, and 17 ml of a 10% solution of ammonia in absolute ethanol was heated in a sealed tube in a boiling water bath for 12 hours. Alcohol and excess of ammonia were then removed under reduced pressure, and dry ether was added to the residue. The precipitate formed (4.8 g) was filtered off; it was found to be ammonium hydrogen phenylphosphonite (III). Dry hydrogen chloride was passed through the ether solution. The oil that separated crystallized partially after it had stood for three days. After prolonged rubbing with fresh portions of dry ether, the oil solidified completely. Recrystallization from a mixture of alcohol and ether yielded 5.4 g (26%) of a substance melting at 164-165°.

		Found %:	P 9.9; 9.7;		N 4.6; 4.5		
$C_{15}H_{19}NPO_2Cl$(VI).	Calculated %:	P 9.9;		N 4.5			

When the reaction is carried out under milder conditions, the main product is ethyl (α-hydroxybenzyl)phenylphosphinate (VIII). Thus, the same mixture of reactants was heated for five hours, and 3 g of ethyl (α-hydroxybenzyl)phenylphosphinate, m.p. 75°, was isolated.

		Found %:	C 65.9; 65.5;		H 5.7; 5.8;		P 11.1; 11.1
$C_{15}H_{17}PO_3$.	Calculated %:	C 65.2;		H 6.2;		P 11.2;	

In this experiment the yield of the hydrochloride of ethyl (α-aminobenzyl)phenylphosphinate was only about 10%.

(α-Aminobenzyl)phenylphosphinic Acid (VII)

A mixture of 4 g of the hydrochloride prepared as above and 80 ml of 1 : 1 hydrochloric acid was heated at 125-130° in two sealed tubes for three hours. The contents of the tubes were then evaporated down until a residue of constant weight was obtained. Recrystallization of the residue from 50% ethanol yielded 1.6 g (48%) of a colorless crystalline substance. m.p. 218°. The substance crystallized with one molecule of water of crystallization.

	Found %:	C 58.8; 58.8; H 5.8; 6.1; P 11.5; 11.2; N 5.3; 5.2; H_2O 5.8; 6.7
$C_{13}H_{12}NPO_3 \cdot H_2O$(VII).	Calculated %:	C 58.9; H 6.1; N 5.3; P 11.7; H_2O 6.8

Hydrochloride of Ethyl (1-Aminocyclohexyl)phenylphosphinate (IX)

A mixture of 6.5 g of cyclohexanone, 11.5 g of ethyl hydrogen phenylphosphonite, and 17 ml of a 10% solution of ammonia in absolute alcohol was heated in sealed tubes in a boiling water bath for 12 hours. Alcohol and excess of ammonia were distilled off, and dry ether was added to the residue. The crystals that had formed in the solution by the next day were filtered off (1.2 g); they were found to be ammonium hydrogen phenylphosphonite. Dry hydrogen chloride was passed through the ether solution and an oil separated which partially crystallized after standing for three days. The oil was repeatedly rubbed out in presence of fresh portions of ether, and finally a free-running solid was obtained, which was reprecipitated from an alcohol-ether mixture. The yield was 6.2 g (31%). The substance had a double melting point, 149° and 193°. It was hygroscopic.

	Found %:	N 4.6; 4.4; P 9.8
$C_{14}H_{23}NPO_2Cl$ (IX)	Calculated %:	N 4.6; P 10.2

Picrate of Ethyl (1-Aminocyclohexyl)phenylphosphinate (X)

A saturated solution of sodium carbonate was added to a solution of 5.0 g of the hydrochloride (IX) in 10 ml of water. The layer that separated was removed, and the remaining liquid was extracted with ether, the extract being added to the liquid already removed. The ether solution was dried with sodium sulfate. After removal of ether, 4.3 g of the oily ethyl (1-aminocyclohexyl)phenylphosphinate was obtained. An ethereal solution of picric acid was added, and the picrate was precipitated. Recrystallization from alcohol yielded yellow crystals, m.p. 168°.

	Found %:	N 2.8; 2.8; P 6.4; 6.3
$C_{18}H_{25}N_4PO_9$.	Calculated %:	N 2.8; P 6.2

(1-Aminocyclohexyl)phenylphosphinic Acid (XI)

A mixture of 3 g of the hydrochloride of ethyl (1-aminocyclohexyl)phenylphosphinate and 60 ml of 1 : 1 hydrochloric acid was heated in two sealed tubes at 115-125° for three hours. The contents were then evaporated down on a boiling water bath to a residue of constant weight free from the odor of HCl. The solid residue was recrystallized from water, and 2.1 g (75%) of a colorless crystalline substance melting at 212° was obtained. It crystallized with one molecule of water.

	Found %:	C 56.2; 56.2; H 7.9; 8.0; P 12.3; 12.6; N 5.4; 5.3; H_2O 7.5
$C_{12}H_{18}PNO_3 \cdot H_2O$ (XI).	Calculated %:	C 56.0; H 7.8; P 12.1; N 5.4; H_2O 7.0

An aqueous solution of the substance was neutral to litmus.

(1-Acetamide-1-methylethyl)phenylphosphinic Acid (XII)

A mixture of 0.9 g of (1-amino-1-methylethyl)phenylphosphinic acid and 8 g of acetic anhydride was heated under reflux in a boiling water bath for 90 minutes. Acetic anhydride was removed under reduced pressure, and the residue - a yellowish glassy mass - solidified when rubbed out with dry ether. Crystallization from alcohol yielded 0.85 g (78%) of a colorless substance, m. p. 197-198°.

	Found %:	C 54.9; 54.7; H 6.6; 6.7; P 12.8; 12.5; N 5.7; 5.6
$C_{11}H_{16}PNO_3$.	Calculated %:	C 54.8; H 6.6; P 12.9; N 5.8

Ethyl (1-Hydroxy-1-methylethyl)phenylphosphinate (XIV)

Sodium ethoxide solution (0.4 ml) was added dropwise to a mixture of 17 g of ethyl hydrogen phenylphosphonite and 5.8 g of acetone. The temperature of the mixture rose to 70°. The mixture was heated for 30 minutes in a boiling water bath. On the next day the solid precipitate was filtered off and recrystallized from absolute ethanol.

The product was 5.2 g (23%) of colorless crystals, m.p. 94-96°, readily soluble in water, alcohol, and benzene.

	Found %:	C 58.1; 58.0;	H 7.4; 7.6;	P 13.5; 13.7
$C_{11}H_{17}PO_3$.	Calculated %:	C 57.9;	H 7.5;	P 13.6;

(1-Hydroxy-1-methylethyl)phenylphosphinic Acid (XIII)

A. Reaction of Nitrous Acid with (1-Amino-1-methylethyl)phenylphosphinic Acid. Oxides of nitrogen were passed through a solution, cooled with ice water, of 2 g of (1-amino-1-methylethyl)phenylphosphinic acid in 25 ml of water until nitrogen ceased to be evolved (two hours). Toward the end of the reaction the solution was heated at 40° for 15 minutes. The solution was evaporated down under reduced pressure at 40°. The residue was dried in a vacuum desiccator over caustic alkali and phosphoric oxide. Crystallization from a mixture of chloroform and petroleum ether yielded 0.8 g (40%) of colorless crystals, m.p. 163°.

	Found %:	C 54.2; 54.2;	H 6.5; 6.4;	P 15.5
$C_9H_{13}PO_3$.	Calculated %:	C 54.0;	H 6.5;	P 15.5

The equivalent weight was determined by titration to phenolphthalein with 0.1 N NaOH. The value obtained was 199 (value calculated, 200).

B. Hydrolysis of Ethyl (1-Hydroxy-1-methylethyl)phenylphosphinate (XIV). A mixture of 2.3 g of ethyl (1-hydroxy-1-methylethyl)phenylphosphinate and 45 ml of 1 : 1 hydrochloric acid was heated in two sealed tubes at 120-125° for three hours. The liquid was evaporated down on a boiling water bath, heating being continued until the odor of hydrogen chloride had disappeared completely, and the residue was recrystallized from benzene. The product was 1 g (50%) of a colorless crystalline substance, m.p. 162-163°.

	Found %:	C 54.0; 54.1;	H 6.5; 6.4;	P 15.7; 15.6
$C_9H_{13}PO_3$.	Calculated %:	C 54.0;	H 6.5;	P 15.5;

The equivalent weight was determined by titration to phenolphthalein with 0.1 N NaOH. The value obtained was 198 (value calculated, 200).

There was no depression in a mixture melting point test with the substance obtained by the action of nitrous acid on (1-amino-1-methylethyl)phenylphosphinic acid.

SUMMARY

1. The reaction between monoesters of phenylphosphonous acid, ketones or aldehydes, and ammonia has been studied. (1-Amino-1-methylethyl)-, (1-amino-1-methylpropyl)-, (α-aminobenzyl)-, and (1-aminocyclohexyl)-phenylphosphinic acids have been prepared, and also the hydrochlorides of their ethyl esters.

2. With (1-amino-1-methylethyl)phenylphosphinic acid as working example, the structure of the synthesized compounds has been proved. (1-Amino-1-methylethyl)phenylphosphinic acid can be converted in the usual way into its acetyl derivative, and treatment with nitrous acid converts it into the corresponding hydroxy acid.

3. A mechanism has been proposed for the reaction: it is considered that the alkyl hydrogen phenylphosphonite ionizes under the influence of ammonia, and its anion then adds to the carbonyl compound; this is followed by replacement of the hydroxy group by amino.

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Received January 15, 1954

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MECHANISM OF THE FORMATION OF POLYPHENYLPOLYSILOXANES FROM TERFUNCTIONAL "MONOMERS"

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Modern methods of preparing organopolysiloxanes are based on the hydrolysis and condensation reactions undergone by bi- and ter-functional alkylhalo- and alkylalkoxy-silanes. In these processes, condensation is generally not separable from hydrolysis, for when these monomeric compounds are treated with water immediate formation occurs of polymeric substances of greater or less degree of polymerization.

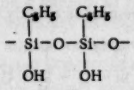
The mechanism of the formation of organopolysiloxanes from bifunctional "monomers" has been the subject of several investigations, in which polymer formation has been regarded as a stepwise condensation process [1-6] or as a mixed condensation-polymerization process [7]. Investigations on the reactions of terfunctional monomers have been much fewer.

Data in the literature refer only to the partial hydrolysis of alkyltriethoxysilanes in presence of an insufficient amount of water, i.e., under such conditions that one of the functional groups does not take part in the hydrolysis reaction [8]. There are no definite data in the literature about the structure, and mechanism of formation, of polymers obtained when terfunctional monomers are hydrolyzed with excess of water. Recent work with the object of isolating monomeric substances or primary condensation products in the hydrolysis of terfunctional monomers did not yield positive results [9]. The hydrolysis of dialkyldichlorosilanes results in the formation of a mixture of cyclic and linear polymers. The relative amounts of cyclic and linear molecules in the polymer depend on various conditions and may vary over a wide range. It may be stated as a general rule that increase in the concentration of the acid used for the hydrolysis leads to an increase in the yield of cyclic products.

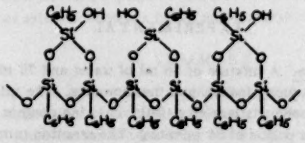
The object of the present investigation was the eludication of the structure of polymers formed from terfunctional monomers by hydrolysis in strongly acid and weakly acid media. With this in view we have hydrolyzed trichlorophenylsilane with various amount of water in presence of diethyl ether as solvent, and we have characterized the resulting polymers by their silicon and hydroxyl contents and by the relative viscosity of a 30% solution of the polymer in toluene. The results are given in the table.

These results are in obvious conflict with usually accepted ideas about the linear or three-dimensional structure of a polymer resulting from the hydrolysis of a terfunctional monomer.

If, in fact, we regard the polymer formed when trichlorophenylsilane is hydrolyzed in an acid medium in presence of solvent as linear, its structure should be:



The repeating unit of such a polymer should contain 20.29% of silicon and 12.31% of hydroxyl groups, and these figures are not in accord with the analytical results. The possibility of formation of cross links between the linear molecules must be excluded, since these polymers of low hydroxyl content are very readily soluble in most organic solvents, including benzene, acetone, diethyl ether, propyl alcohol, butyl alcohol, toluene, and ethyl acetate – they are insoluble only in methanol and ethanol. On the basis of the results obtained we consider that the polymers that we have obtained contain internal rings in their structure, as, for example, in the following scheme:

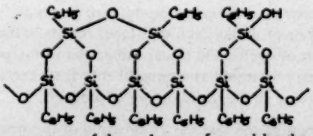


TABLE

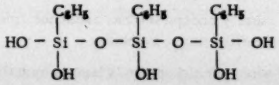
Expt. No.	Acidity of aqueous layer (%)	Silicon content of polymer(%)	Hydroxyl content of polymer (%)	Time of efflux of a 30% polymer solution (seconds)
1	21.2	22.61	2.20	519
2	14.1	21.83	1.97	188
3	9.2	22.08	2.02	143
4	7.9	22.63	2.38	144
5	6.7	22.25	2.24	130

The repeating unit of such a polymer should contain 21.23% of silicon and 4.29% of hydroxyl groups, and although these figures are more in accord with the experimental values, they are nevertheless different. In a polymer of this structure, however, further condensation of hydroxyl groups can occur with the formation of more intramolecular oxygen bridges, and without conversion to a polymer of three-dimensional structure. We do not altogether reject the possibility of the occurrence of some intermolecular condensation between hydroxyl groups, but consider this process less probable, because of steric hindrance by the aromatic nucleus attached to the silicon atom. Indirect confirmation of these views is provided by the fact that, in spite of their high functionality, polyphenylpolysiloxane resins, when heated for a long time at 200°, behave like thermoplastic polymers.

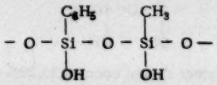
Hence, when terfunctional organosilicon monomers are hydrolyzed in a strongly acid medium in presence of solvent, polymers containing internal rings are formed. The possibility of cross-linking between polymer molecules is directly dependent on the size of the organic radical. With increase in its size and in its steric hindrance effect, intramolecular condensation tends to become predominant. We consider that the organosilicon polymer formed by the hydrolysis of trichlorophenylsilane with water in presence of diethyl ether has the following structure:



We were interested also in the structure of the polymers formed by the hydrolysis of triacetoxyphenylsilane (phenylsilanetriol triacetic ester), since the acid formed is then the weak acetic acid, giving a low hydrogen ion concentration in the aqueous phase. At this low acidity we expected that linear polymers would be formed. As a result of our experiments on the hydrolysis of triacetoxyphenylsilane we isolated the linear trimer 1,3,5-triphenyltrisiloxane-1,1,3,5,5-pentol:



Cohydrolysis of triacetoxyphenylsilane and triacetoxymethylsilane yielded linear polymers, which, according to the analytical results for silicon and hydroxyl groups, corresponded exactly to the following structure:



These polymers, formed by hydrolysis of triacetoxyalkyl- and triacetoxyaryl-silanes and containing a considerable number of hydroxyl groups, differ qualitatively from the analogous polymers prepared by the hydrolysis of alkyltrichlorosilanes in many of their properties, of which the most characteristic is solubility. They are, for example, highly soluble in ethanol and methanol, and some of them (polymethylpolysiloxanes) are insoluble in benzene, although the products of the hydrolysis of trichloromethylsilane are readily soluble in benzene.

EXPERIMENTAL

Hydrolysis of Trichlorophenylsilane. A mixture of 50 ml of water and 75 ml of diethyl ether was prepared in a three-necked flask fitted with stirrer, dropping funnel, and thermometer. The mixture was stirred continuously, and a solution of 42.3 g (0.2 mole) of trichlorophenylsilane (b.p. 201°, chlorine content 50.35%) in 75 ml of diethyl ether was added from the dropping funnel over a period of 30 minutes. The reaction temperature was 18-20° during the whole of this time. The mixture was then stirred for a further 30 minutes, after which the organic layer was separated

from the aqueous layer, washed with water until neutral, and dried with sodium sulfate. The solution was filtered, ether was removed under reduced pressure, and the last traces of solvent were removed from the polymer in a vacuum dryer at 40° and a residual pressure of 20 mm until constant weight was attained.

Other experiments on the hydrolysis of trichlorophenylsilane were carried out by the same procedure, the only difference being in the amount of water taken for the hydrolysis of the same amount of trichlorophenylsilane in presence of the same amount of ether. The amounts of water taken in the second, third, fourth, and fifth experiments were 125, 200, 250, and 300 ml respectively. In all of these experiments the products were colorless brittle polymers, soluble in benzene, ether, acetone, and ethyl acetate, but insoluble in ethanol.

The hydroxyl contents of these polymers were determined by the Chugaev-Tserevitinov method. Silicon was determined by wet combustion of a weighed sample with fuming sulfuric acid and calcination of the residue to constant weight. The analytical results are given in the table.

Triacetoxyphenylsilane. Triacetoxyphenylsilane was prepared by a slight modification of the procedure described previously for the preparation of triacetoxymethylsilane (10). A mixture of 211.5 g (1 mole) of trichlorophenylsilane and 306 g (3 moles) of acetic anhydride was allowed to stand at room temperature for 12 hours, and was then heated in a flask fitted with a dephlegmator and condenser set for distillation, it being arranged that the temperature of the vapor passing into the condenser was not higher than 55°.

When 220 g (about 2.8 moles) of acetyl chloride had collected in the receiver, the residue was transferred to a Claisen flask, and unchanged acetic anhydride and trichlorophenylsilane were distilled off up to a temperature of 85° at 8 mm. When cooled, the reaction product solidified to a crystalline mass. This crystalline product, which was later used in hydrolysis experiments, was analyzed for acetyl and silicon content.

	Found %: $OCOCH_3$ 62.81; Si 9.80
$C_{12}H_{14}O_6Si$.	Calculated %: $OCOCH_3$ 62.73; Si 9.94

Cohydrolysis of Triacetoxyphenylsilane and Triacetoxymethylsilane. A mixture of 70.58 g (0.25 mole) of triacetoxyphenylsilane and 55.05 g (0.25 mole) of triacetoxymethylsilane was prepared in a three-necked flask fitted with stirrer, dropping funnel, and thermometer. The mixture was stirred, and 9 g (0.5 mole) of water was added. The temperature of the reaction mixture then rose to 45°. The mixture was cooled, and 400 ml of ether and 200 ml of water were added to complete the hydrolysis. The mixture was stirred for 30 minutes and the organic layer was then separated, washed until neutral, and dried with sodium sulfate. The solution was filtered, ether was removed at a residual pressure of 25 mm and up to a temperature of 50°, and residual solvent was removed from the polymer in a vacuum dryer at 40° and 20 mm until constant weight was attained. The product was 45 g (53.5%) of a resin, soluble in ethanol, methanol, ether, and acetone.

	Found %: Si 26.18; OH 14.33
$C_7H_{10}O_4Si$.	Calculated %: Si 26.16; OH 15.88

Hydrolysis of Triacetoxyphenylsilane and Isolation of Crystalline 1,3,5-Triphenyltrisiloxane-1,1,3,5,5-pentol. Water (250 ml), contained in a three-necked flask fitted with stirrer, dropping funnel, and thermometer, was vigorously stirred under cooling to 0° while a solution of 70.58 g (0.25 mole) of triacetoxyphenylsilane in an equal amount of ether was added. When the hydrolysis was complete, the organic layer was separated, washed until neutral, and dried with sodium sulfate. Solvent was removed at 20° and 15 mm residual pressure, and an opaque, greasy residue was obtained. This was treated with 50 ml of benzene, and the insoluble part, which consisted of fine crystals, was filtered off. The crystalline product was washed twice with benzene and dried in a vacuum desiccator. The yield was 4.7 g (12.3%).

	Found %: Si 19.45; C 49.31; H 4.89; O 26.31
$C_{18}H_{20}O_7Si_3$.	Calculated %: Si 19.44; C 50.00; H 4.63; O 25.93

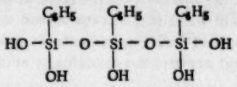
The molecular weight, determined cryoscopically in dioxane, was 433 (calculated value, 432). The substance melted at 113.5-114°, and when it melted, condensation with formation of transparent polymer and separation of water was observed. 1,3,5-Triphenyltrisiloxane-1,1,3,5,5-pentol forms a clear solution in water. When acidified with mineral acids and when heated, its aqueous solution becomes turbid and a precipitate is formed.

SUMMARY

1. It has been shown that, when terfunctional organosilicon monomers are hydrolyzed in an aqueous medium in presence of mineral acids, complex cyclic polymeric products are formed which do not readily pass, when heated, into three-dimensional polymers, since further condensation occurs by two competing reactions—intramolecular de-

hydration and intermolecular condensation. The first reaction predominates when the organic radical attached to silicon is large, and the second when it is small.

2. Hydrolysis of triacetoxyphenylsilane in a weakly acid medium (acetic acid) yielded the crystalline trimer 1,3,5-triphenyltrisiloxane-1,1,3,5,5-pentol:



3. Hydrolysis of terfunctional monomers in a weakly acid medium (in presence of organic acids) results in the formation of linear polymers. This view is confirmed by the isolation of the crystalline product 1,3,5-triphenyltrisiloxane-1,1,3,5,5-pentol and by the analytical data on the more complex polymers.

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Received February 23, 1954

SYNTHESIS OF SOME ORGANIC DERIVATIVES OF MONO- AND DI-THIONOPYROPHOSPHORIC ACIDS

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Investigations of recent years have shown that esters and alkylamides of pyrophosphoric acid and of its sulfur analogs are effective substances for use in combating agricultural pests. Substances that have now been prepared include various esters of pyrophosphoric and dithionopyrophosphoric acid, tetraethyl monothionopyrophosphate, and alkylamides of pyrophosphoric acid [1]. All of these groups of compounds, however, have not only insecticidal activity, but also toxicity to warm-blooded animals. Pyrophosphoric esters are the most toxic, then follow monothionopyrophosphoric esters, and tetraethyl dithionopyrophosphate and the tetrakis(dimethylamide) of pyrophosphoric acid are of relatively low toxicity.

In the present paper we give the results of experiments on preparation of: ethyl esters, mixed alkyl esters and mixed ester-alkylamides of mono- and di-thionopyrophosphoric acids. The object of the work was the preparation of new insecticides of the thionopyrophosphoric acid series.

The method that we used for the synthesis of these organic derivatives of mono- and di-thionopyrophosphoric acids was essentially that used by Toy [2] for the preparation of tetralkyl dithionopyrophosphates. This method consists in the action of the calculated amount of water on a dialkyl phosphorochloridothionate in presence of pyridine or other base:

$$1.\ (AlkO)_2P(S)Cl + H_2O + C_5H_5N = (AlkO)_2P(S)OH + C_5H_5N \cdot HCl$$

$$2.\ (AlkO)_2P(S)OH + ClP(S)(OAlk)_2 + C_5H_5N = (AlkO)_2P(S)-O-P(S)(OAlk)_2 + C_5H_5N \cdot HCl.$$

The diethyl hydrogen phosphorothionate that we required for our syntheses was prepared not by the decomposition of its acid chloride by water, as in Toy's method, but by the addition of sulfur to diethyl hydrogen phosphite at 60° in presence of an amine, such as pyridine, triethylamine, or diethylaniline:

$$(C_2H_5O)_2POH + S = (C_2H_5O)_2P(S)OH$$

The resulting diethyl hydrogen phosphorothionate was treated with various acid chlorides of organic derivatives of phosphoric acid, for example:

$$(C_2H_5O)_2P(S)OH + ClP(O)[N(CH_3)_2]_2 + (C_2H_5)_3N =$$

$$= (C_2H_5O)_2P(S)-O-P(O)[N(CH_3)_2]_2 + (C_2H_5)_3N \cdot HCl.$$

The known tetraethyl esters of mono- and di-thionopyrophosphoric acids were also prepared by this method.

The insecticidal properties of the synthesized substances were tested on the corn weevil. The weevils were contained in small beakers standing on a rotating disk under a glass bell jar, and they were sprayed with an aqueous solution of the preparation at a definite concentration with the aid of an atomizer and air blower.

The sprayed weevils and the controls were observed over a period of seven days.

Table 1 gives the formulas, physical constants, and yields of the compounds, the amines used for binding hydrogen chloride, and the comparative toxicities to the corn weevil under spray conditions. It will be seen from Table 1 that, with respect to the corn weevil, the effectiveness of the mixed alkyl esters and amide-esters of monothionopyrophosphoric acid (No. 2, 3, 4, 5, 6, and 7) is less than that of tetraethyl monothionopyrophosphate (No. 1). The same is true for the amide-esters of dithionopyrophosphoric acid (No. 9 and 10), as compared with tetraethyl dithionopyrophosphate (No. 8). Compounds No. 1, 4, 8, and 9 were tested on warm-blooded animals. The results of these tests are given in Table 2. Table 2 shows that the mixed dimethylamide-esters of mono- and di-thionopyrophosphoric acids (No. 4 and

TABLE 1

No.	Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	Phosphorus content (%) Found	Phosphorus content (%) Calculated	Yield (%)	Amine	Toxicity to the corn weevil (by spray) Concentration (%)	Toxicity to the corn weevil (by spray) Proportion killed after 7 days (%)
1	$(C_2H_5O)_2P(O)-O-P(S)(OC_2H_5)_2$	127.5–128.5(1)	1.4523	1.1930	20.56 20.31	20.56	72.4 68.3 66.2	Triethylamine-pyridine-diethylaniline	0.005	100
2	$(i\text{-}C_3H_7O)_2P(O)-O-P(S)(OC_2H_5)_2$	125–126 (2)	1.4439	1.1322	18.91 18.88	18.56	52.3	Triethylamine	0.05	75
3	$(C_4H_9O)_2P(O)-O-P(S)(OC_2H_5)_2$	147–149(2)	1.4512	1.1161	17.24 17.38	17.12	30.1	Triethylamine	0.05	100
4	$(CH_3)_2N-P(O)(OC_2H_5)-O-P(S)(OC_2H_5)_2$	120 (1)	1.4593	1.1784	20.46 20.55	20.32	68.6	Triethylamine	0.05	100
5	$(C_2H_5)_2N-P(O)(OC_2H_5)-O-P(S)(OC_2H_5)_2$	143–145(1)	1.4595	1.1402	18.38 18.58	18.65	17.6	Triethylamine	0.05	75
6	$[(CH_3)_2N]_2P(O)-O-P(S)(OC_2H_5)_2$	127–128(1)	1.4719	1.1667	20.46 20.62 S 10.54 10.51	20.59 S 10.52	42.4	Triethylamine	0.1	60
7	$[(C_2H_5)_2N]_2P(O)-O-P(S)(OC_2H_5)_2$	163–166(2)	1.4669	1.0871	16.95 16.87	17.22	13.1	–	–	–
8	$(C_2H_5O)_2P(S)-O-P(S)(OC_2H_5)_2$	134–135(2.5)	1.4775	1.1897	–	–	62.7	Triethylamine	0.05	100
9	$(CH_3)_2N-P(S)(OC_2H_5)-O-P(S)(OC_2H_5)_2$	135 (2)	1.4921	1.1829	19.17 19.24	19.31	53.5	Triethylamine	0.05	70
10	$[(C_2H_5)_2N]_2P(S)-O-P(S)(OC_2H_5)_2$	168.5–170 (3)	–	–	16.3 16.23 S 16.79 16.64	16.48 S 17.02	38.5	–	0.1	45

and 9) are less toxic than tetraethyl mono- and di-thionopyrophosphates (Nos. 1 and 8) respectively. It will be noted that preparation No. 9 is less effective than preparation No. 8 when applied to the corn weevil, but the difference is not significant, for the toxicity of No. 9 to warm-blooded animals is much less than that of No. 8 (replacement of ethoxyl by dimethylamino).

1. Preparation of Diethyl Hydrogen Phosphorothionate

A mixture of 18 g (one molecular proportion) of diethyl hydrogen phosphite and 13.2 g (one molecular proportion) of triethylamine was stirred while 4.17 g (one atomic proportion of sulfur powder was added in portions. The sulfur reacted vigorously with the diethyl hydrogen phosphite and, owing to the evolution of heat, it was necessary to cool the reaction flask with water every now and then. The mixture was then heated for 10–15 minutes at 60°, and all of the sulfur went into solution.

The addition of sulfur to diethyl hydrogen phosphite is less vigorous in presence of pyridine or diethylaniline. When these amines were used, the sulfur was add gradually to a mixture of diethyl hydrogen phosphite and amine at 50–55°, and the mixture was then stirred at 60° for 60–90 minutes.

2. Preparation of Derivatives of Mono- and Di-thionopyrophosphoric Acids

The calculated amount of the acid chloride of an organic derivative of phosphoric acid was added at 30 - 35°

to diethyl hydrogen phosphorothionate, prepared as in the first experiment, containing dissolved amine (triethylamine, pyridine, or diethylaniline); the hydrochloride of the amine separated out.

The thick mass was stirred for 2-3 hours at 35-40°, cooled, and diluted with gasoline (b.p. 75-125°). The precipitate was filtered off. The gasoline was removed under reduced pressure, and the residue was vacuum-distilled.

In this way compounds No. 1, 2, 3, 4, 5, 6, 8, and 9 (Table 1) were prepared. Compounds No. 7 and 10 were prepared by reaction of the corresponding acid chlorides with sodium diethyl phosphorothionate.

TABLE 2

Toxicity of Preparations to White Mice and Guinea Pigs

Compound	White mice (subcutaneously)		Guinea pigs	
	LD50 (mg/kg)	LD100 (mg/kg)	LD50 (mg/kg)	LD100 (mg/kg)
$(C_2H_5O)_2P(O)-O-P(S)(OC_2H_5)_2$ (1)	–	0.25	4	6
$(CH_3)_2N-P(O)(OC_2H_5)-O-P(S)(OC_2H_5)_2$ (4)	2	–	7	10
$(C_2H_5O)_2P(S)-O-P(S)(OC_2H_5)_2$ (8)	–	8	15	40
$(CH_3)_2N-P(S)(OC_2H_5)-O-P(S)(OC_2H_5)_2$ (9)	30	40	40	60

SUMMARY

1. Diethyl hydrogen phosphorothionate has been prepared by the addition of sulfur to diethyl hydrogen phosphite in presence of one of the following amines: triethylamine, pyridine, and diethylaniline.

2. Ethyl esters, some mixed alkyl esters, and some mixed ester-amides of mono- and di-thionopyrophosphoric acids have been synthesized.

3. Tests have been made of the action of the synthesized substances on the corn weevil, and four of them have been tested on white mice and guinea pigs.

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Received January 16, 1954

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SYNTHESIS OF SOME N-SUBSTITUTED DERIVATIVES OF DIETHYL PHOSPHORAMIDATE

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Many organic compounds of phosphorus and nitrogen containing a phosphorus-nitrogen bond (P–N) are known. They are readily prepared, for example by the action of ammonia or an amine on the acid chloride of an organic derivative of a phosphorus acid. In compounds obtained in this way, the hydrogens on the nitrogen can be replaced by various alkyl and aryl radicals.

Amides are known in which one of these hydrogens is replaced by acyl. Such compounds have been prepared in very low yield by the action of phosphorus pentachloride on chloro- or bromo-acetamides [1] and by the action of N-bromoamides of carboxylic acids on sodium dialkyl phosphites [2].

In the present paper we describe two methods for the preparation of diethyl phosphoramidates and phosphoramidites in which various acid residues are attached to nitrogen. One of these methods consists in the action of tetraethyl pyrophosphite on a carboxamide:

$$CH_3CONH_2 + (C_2H_5O)_2P-O-P(OC_2H_5)_2 = CH_3 \cdot CONHP(OC_2H_5)_2 + HOP(OC_2H_5)_2$$

and the second method – in the action of acid chlorides of organic and mineral acids, and also of alkyl halides, on N-sodium derivatives of diethyl N-alkylphosphoramidates.

When diethyl N-monoalkyl- and N-monoaryl-phosphoramidates are treated with sodium, sodium derivatives are formed which are readily soluble in organic solvents:

$$(C_2H_5O)_2\overset{\displaystyle O}{\overset{\|}{P}}-\underset{\displaystyle CH_3}{\underset{|}{NH}} + Na = (C_2H_5O)_2\overset{\displaystyle O}{\overset{\|}{P}}-\underset{\displaystyle CH_3}{\underset{|}{N}}\,Na + H$$

When the latter compounds are treated with halogen-containing compounds, various amide derivatives can be obtained, for example:

$$C_2H_5OCOCl + \underset{\displaystyle CH_3}{\underset{|}{NaN}} - \overset{\displaystyle O}{\overset{\|}{P}}(OC_2H_5)_2 = NaCl + C_2H_5OCON\underset{\displaystyle CH_3}{\underset{|}{}} - \overset{\displaystyle O}{\overset{\|}{P}}(OC_2H_5)_2$$

Similarly, phosgene and diethyl N-methyl-N-sodiophosphoramidate yielded an organophosphorus urea derivative:

$$COCl_2 + 2NaN\underset{\displaystyle CH_3}{\underset{|}{}} - \overset{\displaystyle O}{\overset{\|}{P}}(OC_2H_5)_2 = 2NaCl + (C_2H_5O)_2\overset{\displaystyle O}{\overset{\|}{P}}-\underset{\displaystyle CH_3}{\underset{|}{N}}-CO-\underset{\displaystyle CH_3}{\underset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{P}}(OC_2H_5)_2$$

In this way, by the action of diethyl N-methyl-N-sodiophosphoramidate on ethyl chloroformate, diethylcarbamoyl chloride, phosgene, ethyl phosphorodichloridite, sulfur dichloride, methylene dibromide, and ethyl bromoacetate, the corresponding derivatives of diethyl phosphoramidate were obtained. The formulas of these compounds, and their physical constants and yields are given in the table. All the substances in the table are colorless liquids; some of them are mobile, others are more viscous. They are soluble in water and organic solvents. Tests on corn weevils showed that these compounds are not insecticides.

EXPERIMENTAL

1. Action of Tetraethyl Pyrophosphite on Acetamide

Acetamide (2.8 g) was added to 12.2 g of tetraethyl pyrophosphite contained in an Arbuzov distillation flask, and the mixture was heated for 15 minutes at a bath temperature of 120°. As a result of several distillations, two main fractions were obtained: Fraction I, b.p. 70-71° at 10 mm, n_D^{20} 1.4085; d_4^{20} 1.0713, was diethyl hydrogen phosphite (one of the reaction products); the yield was 5 g (76.6%). Fraction II, b.p. 88.5-89.5° at 3 mm, was obtained in 40.4% yield (3.4 g); it had n_D^{20} 1.4375.

$C_6H_{14}PO_3N$. Found %: P 17.36; 17.11
Calculated %: P 17.31

The substance is a colorless liquid smelling of acetamide. It is soluble in water and organic solvents.

2. Action of Ethyl Chloroformate on Diethyl N-Methyl-N-sodiophosphoramidate

Preparation of Diethyl N-Methyl-N-sodiophosphoramidate Required in This and Subsequent Preparations. The reaction was carried out in a flask fitted with stirrer, reflux condenser, and dropping funnel. Gasoline (b.p. 75-125°) was poured into the flask, the volume taken being 6-6.5 times as great as the volume of the diethyl N-methylphosphoramidate to be taken for reaction. A certain excess of sodium was added in the form of lumps, and the ester-amide was added dropwise at room temperature. Reaction was vigorous. The sodium derivative of the amide remained in solution. When the addition was complete, the flask was heated in a bath at 60-70° for 1.5-2 hours. When reaction was complete, as indicated by the cessation of evolution of hydrogen bubbles, the excess of sodium was removed. The amount of sodium that reacted was exactly the amount calculated.

Reaction with Ethyl Chloroformate. Ethyl chloroformate (10 g) was added from a dropping funnel to a water-cooled gasoline solution of diethyl N-methyl-N-sodiophosphoramidate prepared from 15.5 g of the amide and 2.13 g of sodium. Sodium chloride separated immediately. In order to complete the reaction, the reaction mixture was heated in a bath at 60-70° for 30-40 minutes. The mixture was cooled, the sodium chloride was centrifuged off, and the gasoline was distilled off under somewhat reduced pressure.

The residue of 18.2 g (82.3%) was fractionated. Two fractionations from an Arbuzov flask yielded 12 g (54.3%) of a substance boiling at 95-96° (1.5 mm) and having n_D^{20} 1.4299; d_4^{20} 1.1311.

Found %: P 13.17; 13.04

$C_8H_{18}PO_5N$. Calculated %: P 12.97

The substance is a colorless odorless mobile liquid, readily soluble in water and organic solvents.

TABLE

Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	Yield (%)
$CH_3CONHP(OC_2H_5)_2$	88.5–89.5 (3)	1.4375	–	40.4
$C_2H_5OCON(CH_3)PO(OC_2H_5)_2$	95 – 96 (1.5)	1.4299	1.1311	54.3
$(C_2H_5)_2NCON(CH_3)PO(OC_2H_5)_2$	112 (1)	1.4478	1.0849	46.1
$(C_2H_5O)_2P(O)N(CH_3)CON(CH_3)P(O)(OC_2H_5)_2$	145–146.5 (0.5)	1.4505	1.2019	21.9
$C_2H_5OP[N(CH_3)PO(OC_2H_5)_2]_2$	170 (0.5)	1.4569	1.1725	19.6
$(C_2H_5O)_2P(O)N(CH_3)SN(CH_3)P(O)(OC_2H_5)_2$	161–163 (2)	1.4600	1.1908	37.8
$(C_2H_5O)_2P(O)N(CH_3)CH_2N(CH_3)P(O)(OC_2H_5)_2$	149–150 (1)	1.4394	1.1309	11.5
$C_2H_5OCOCH_2NPO(OC_2H_5)_2$ (CH₃)	112–114 (2)	1.4295	1.1048	34
$C_2H_5OCOCH_2NHP(O)(OC_2H_5)_2$	135.5 (1)	1.4390	1.1495	74

3) Action of Diethylcarbamoyl Chloride on Diethyl N-Methyl-N-sodiophosphoramidate

The acid chloride (8 g) was added to a gasoline solution of sodioamide prepared form 9.86 g of diethyl N-methylphosphoramidate and 1.35 g of sodium. The yield of crude product was 13.1 g (81.2%), and after three distillations 7.3 g (46.1%) of a substance boiling at 112-113° (1 mm) was obtained; it had n_D^{20} 1.4478; d_4^{20} 1.0849.

Found %: P 11.86; 11.74

$C_{10}H_{23}PO_4N_2$. Calculated %: P 11.65

The substance is a colorless, odorless mobile liquid, soluble in water.

4) Action of Phosgene on Diethyl N-Methyl-N-Sodiophosphoramidate.

A solution of 5.4 g of phosgene in 12 ml of toluene was added to a gasoline solution of diethyl N-methyl N-

sodiophosphoramidate prepared from 17.4 g of amide and 2.4 g of sodium. The yield of crude product, a mobile yellow liquid, was 15 g (82%). Distillation yielded Fraction I (3.8 g), b.p. 90-145° (1 mm) and Fraction II (8.5 g), b.p. 145-160° (1 mm).

Fraction II yielded 4.1 g (21.9%) of a substance boiling at 145-146.5° (0.5 mm) and having n_D^{20} 1.4505 and d_4^{20} 1.2019.

Found %: P 17.31; 17.07

$C_{11}H_{28}P_2O_7N_3$. Calculated %: P 17.22

The substance is a colorless, odorless viscous liquid, readily soluble in water and organic solvents.

5. Action of Ethyl Phosphorodichloridite on Diethyl N-Methyl-N-sodiophosphoramidate

The substances taken for reaction were 6.6 g of diethyl phosphorodichloridite, 15 g of diethyl N-methylphosphoramidate, and 2.06 g of sodium. The yield of crude product was 14.9 g (81.4%). Two distillations from an Arbuzov flask yielded 3.6 g (19.6%) of pure product boiling at 170° (1 mm); it had n_D^{20} 1.4569; and d_4^{20} 1.1725.

Found %: P 22.63; 22.75

$C_{12}H_{28}O_7P_3N_2$. Calculated %: P 22.79

The substance is a fairly mobile, colorless, odorless liquid, soluble in water and organic solvents.

6. Action of Sulfur Dichloride on Diethyl N-Methyl-N-sodiophosphoramidate

The substances taken for reaction were 15 g of diethyl N-methylphosphoramidate, 2.34 g of sodium, and 5.23 g of sulfur dichloride. The yield of crude product (a dark-red liquid) was 15.1 g (81.5%).

The first fractionation from an Arbuzov flask yielded:

Fraction I, b.p. 96-160°; 3 g
Fraction II b.p. 160-172°, 10 g

Fraction II yielded 7 g (37.8%) of a substance boiling at 161-163° (2 mm) and having n_D^{20} 1.4600; d_4^{20} 1.1908.

Found %: P 16.62; 16.74

$C_{10}H_{28}O_6P_2SN_2$. Calculated %: P 17.03

The substance is a fairly mobile, odorless, yellow liquid, soluble in organic solvents and in water.

7. Action of Methylene Dibromide on Diethyl N-Methyl-N-sodiophosphoramidate

Methylene dibromide (9.16 g) was added to a gasoline solution of diethyl N-methyl-N-sodiophosphoramidate prepared from 17.6 g of amide and 2.42 g of sodium. Reaction began at a bath temperature of about 70°. The reaction mixture was heated at a bath temperature of 85-95° with mechanical stirring for 90 minutes. The yield of crude product (a mobile yellow liquid) was 13 g (71.4%).

The first fractionation from an Arbuzov flask yielded:

Fraction 1, b.p. 60-120° (2 mm): 4.1 g
Fraction 2, b.p. 120-150° (1 mm): 6 g
Residue 1.5 g

Fraction I was distilled, but no pure substance was isolated. Distillation of Fraction II yielded 2.1 g (11.5%) of a substance boiling at 149-150° (1 mm) and having n_D^{20} 1.4394; d_4^{20} 1.1309.

Analysis of Fraction II, b.p. 149-150° (1 mm):

Found %: P 18.01; 17.78

$C_{11}H_{28}O_6P_2N_2$. Calculated %: P 17.91

The substance is a colorless, odorless, mobile liquid.

8. Action of Ethyl Bromoacetate on Diethyl N-Methyl-N-sodiophosphoramidate

The substances taken for reaction were 15.36 g of ethyl bromoacetate, 15 g of diethyl N-methylphosphoramidate, 2.1 g of sodium and gasoline as solvent. After the ethyl bromoacetate had been added to the sodioamide, the reaction mixture was kept at room temperature for one hour and at 60-80° in a bath for 30 minutes. The yield of crude product (a dark-brown liquid) was 18.5 g (81.5%).

The first distillation (at 2 mm) yielded:

Fraction I,	b.p. 108°; 2.2 g
Fraction II,	b.p. 108-115°; 11.5 g
Residue	4 g

Distillation of Fraction II yielded 7.7 g (34%) of a substance boiling at 112-114° (2 mm) and having n_D^{20} 1.4295; d_4^{20} 1.1048.

	Found %	P 12.26; 12.47
$C_9H_{20}O_5PN$.	Calculated %	P 12.25

The substance is a colorless odorless liquid soluble in water.

9. Action of Diethyl Phosphorochloridate on the Ethyl Ester of Glycine

One molecular proportion (17.58 g) of diethyl phosphorochloridate was added to 21.7 g (2.07 molecular proportions) of glycine ethyl ester in ether solution. The mixture was stirred for one hour at room temperature, and the precipitate of the hydrochloride of glycine ester was filtered off and washed with ether. The residue after removal of solvent was 26.6 g.

Two distillations from an Arbuzov flask yielded 18 g (74%) of a product boiling at 135.5° (1 mm) and having n_D^{20} 1.4390; d_4^{20} 1.1495.

	Found %	P 13.15; 13.16
$C_8H_{18}O_5PN$.	Calculated %	P 12.97

The substance is a colorless odorless viscous liquid, soluble in water and organic solvents.

SUMMARY

Some N-substituted derivatives of diethyl phosphoramidate are described. They were prepared by the action of various halogen compounds on the N-sodium derivative of diethyl N-methylphosphoramidate.

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Received January 16, 1954

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SYNTHESIS OF AMIDES OF ORGANIC DERIVATIVES OF PHOSPHORIC ACID

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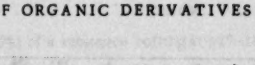
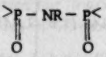
Studies of the insecticidal properties of organic derivatives of pyrophosphoric acid and its sulfur analogs have shown that compounds of this type are very effective for use against many agricultural pests [1]. In these compounds, which are of the anhydride type, two phosphorus atoms are linked through oxygen or sulfur:

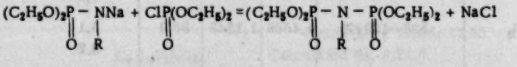


We considered that it would be interesting to synthesize similar compounds in which two phosphorus atoms would be linked through nitrogen:



and to investigate their insecticidal properties.

Compounds of this type can be prepared by the action of acid chlorides of organic derivatives of phosphoric, phosphorothionic, and other acids on N-sodium derivatives of diethyl N-alkylphosphoramidates, for example:



When diethyl N-monoalkyl- and N-monoaryl-phosphoramidates are treated with sodium, they readily yield sodium derivatives that are very soluble in organic solvents. In our experiments we used gasoline (b.p. 75-125°), or on one occasion benzene, as solvent. By the reaction referred to above we have prepared several substances of the required type.

The synthesized substances were tested for insecticidal effect on corn weevils. These tests were carried out as follows. Small beakers containing corn weevils were placed on a rotating disk situated under a glass bell jar, and the weevils were then sprayed, by the aid of an air blower and atomizer, with an aqueous solution of the preparation at a definite concentration. Observations were made on the sprayed weevils and on the controls for a period of seven days. The formulas of the compounds and their physical constants, yields, and comparative toxicity for the corn weevil are given in the table. For purposes of comparison, the table gives the result of the same toxicity test for tetraethyl monothionopyrophosphate (No. 10), which is a well known and very effective insecticide, but is unsuitable for extensive use owing to its high toxicity to warm-blooded animals.

The substances described in the table are colorless mobile liquids, soluble in water and organic solvents. As indicated in the table, the substances that we have prepared are lower in insecticidal power than tetraethyl monothionopyrophosphate (No. 10). The most effective was No. 8, the tetraethyl ester of bis[phosphoric acid] butylamide. In aqueous solution at a concentration of 0.05% it killed all the weevils in four hours; at 0.1% – in two hours. This preparation was not obtained in the pure state, and the technical product was used in the test. It is possible that its high insecticidal power, as compared with other compounds of the same type, was derived not from the substance itself, but from impurities. Preparation No. 5 – the tetraethyl ester of the mixed methylamide of phosphoric and phosphorothionic acids – had a very low toxicity.

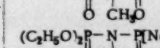
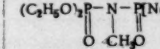
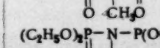
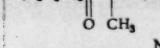
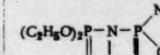
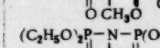
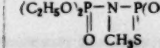
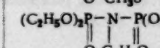
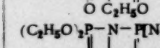
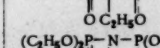
EXPERIMENTAL

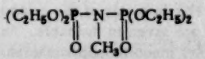
Preparation of Diethyl N-Alkyl-N-sodiophosphoramidates

The reaction was carried out in a flask fitted with stirrer, reflux condenser, and dropping funnel. Gasoline (b.p. 75-125°) was poured into the flask, the volume taken being 6-6.5 times as great as the volume of the amide to be taken for reaction. A certain excess of sodium was added in the form of lumps, and the diethyl N-alkylphosphoramidate added dropwise from the funnel. Reaction set in immediately at room temperature. When the addition

of amide was complete, the flask was heated in a water bath for 1,5-2 hours. When reaction was complete, the solution of the alkylsodioamide was cooled, and the excess of sodium was removed. Exactly the calculated amount of sodium reacted.

TABLE

No.	Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	Yield (%)	Toxicity to the corn weevil (by spray)	
						Concentration (%)	Proportion killed after 7 days
1		138–139 (3)	1.4353	1.1666	46.3	0.05	90
2		147–149 (3)	1.4621	1.0452	35	0.1	85
3		104–106 (1)	1.4435	1.1045	43.4	0.1 0.2	60 90
4		139–141 (1.5)	1.4453	1.3831	62	0.2	80
5		120 (1)	1.4656	1.0420	36.5	0.1	25
6		123–124 (1)	1.4359	1.1468	52.15	0.1 0.2	80 100
7		138–139 (2)	1.4609	1.1345	50.9	0.1 0.2	60 100
8		Technical product	–	–	–	0.01 0.05 0.1	80 100 100
9		Technical product	–	–	–	0.1	60
10		127.5–128.5 (1)	1.4523	1.1930	–	0.005	100

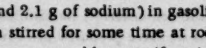
1. Tetraethyl Ester of Bis[phosphoric acid] Methylamide 

Diethyl phosphorochloridate was added to a stirred water-cooled solution of diethyl N-methyl-N-sodiophosphoramidate (prepared from 15 g of the amide and 2.1 g of sodium) in gasoline. The acid chloride was added over a period of 20 minutes, and the mixture was then stirred for some time at room temperature and for 20-30 minutes at a bath temperature of 60°. Sodium chloride was removed by centrifugation, solvent was distilled off under reduced pressure, and the remaining 23.5 g (86.3%) of liquid was distilled. Two distillations from an Arbuzov flask yielded 12.6 g (46.3%) of a pure fraction boiling at 138-139° (3 mm) and having n_D^{20} 1.4353; d_4^{20} 1.1666.

Found %: P 20.7; 20.71

$C_9H_{23}P_2NO_5$. Calculated %: P 20.46

The substance is a very mobile, colorless, odorless liquid, soluble in water and ether.

2. Diethyl Ester of the Mixed Methylamide of Phosphoric and N, N, N', N'-Tetramethylphosphorodiamidic Acids 

The compound was prepared by the action of 15 g of N,N,N',N'-tetramethylphosphorodiamidic chloride on diethyl N-methyl-N-sodiophosphoramidate prepared in gasoline solution from 14.7 g of the amide and 2.02 g of sodium. The crude product, amounting to 22.2 g (83.7%), was distilled at a residual pressure of 2.5 mm from an Arbuzov flask, and yielded the fractions:

Fraction I, b.p. 111-142°; 4 g
Fraction II, b.p. 142-144°; 1.5 g
Fraction III, b.p. 144-148°; 13.9 g
Residue 2 g

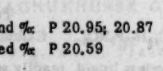
Distillation of Fraction III yielded 9.3 g (35%) of a substance boiling at 147-149° (3 mm) and having n_D^{20} 1.4621; d_4^{20} 1.0452.

Analysis of the fraction boiling at 147-149° (3 mm):

Found %: P 20.95; 20.87
$C_9H_{25}P_3N_3O_4$. Calculated %: P 20.59

The substance is a very mobile, colorless liquid, readily soluble in water and gasoline.

3. Tetraethyl Ester of the Mixed Methylamide of Phosphoric and Phosphorous Acids



The substances taken for reaction were 15 g of diethyl N-methylphosphoramidate, 2.1 g of sodium, and 14.1 g of diethyl phosphorochloridite. The reaction was carried out in gasoline. The yield of crude product, a dark-yellow liquid, was 22.2 g (86%). The first fractionation from an Arbuzov flask at 2 mm – yielded:

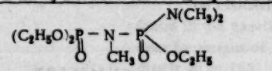
Fraction I, b.p. 42-110°; 2 g
FractionII, b.p. 110-117°; 17.5 g
Residue 2 g

Distillation of Fraction II (17.5 g) yielded 11.2 g (43.4%) of pure product; b.p. 104-106° (1 mm); n_D^{20} 1.4435; d_4^{20} 1.1045.

Found %: P 21.36; 21.35
$C_9H_{23}P_2NO_5$. Calculated %: P 21.6

The substance is a very mobile, colorless liquid having a feeble odor of a phosphorous ester. It is soluble in water.

4. Triethyl Ester of the Mixed Methylamide of Phosphoric and N,N-Dimethylphosphoramidic Acids.

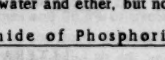


This was prepared similarly to the preceding compound from 15.6 g of diethyl N-methylphosphoramidate, 2.15 g of sodium, and 16.1 g of ethyl N,N-dimethylphosphoramidochloridate. The yield of crude product was 24.1 g (85.4%). Two distillations yielded 17.5 g (62.%) of a fraction boiling at 139-141° and having n_D^{20} 1.4453; d_4^{20} 1.3831.

Found %: P 20.51; 20.46
$C_9H_{24}P_2N_3O_5$. Calculated %: P 20.52

The substance is a very mobile colorless liquid, soluble in water and ether, but not readily soluble in gasoline.

5. Tetraethyl Ester of the Mixed Methylamide of Phosphoric and Phosphorothionic Acids.



The substances taken for reaction were diethyl phosphorochloridothionate (13 g), diethyl N-methylphosphoramidate (11.5 g), and sodium (1.58 g). The conditions were as in the preceding experiments. The yield of crude product, a dark-yellow liquid, was 19 g (86.7%). The first fractionation (1.5 mm) yielded:

Fraction I, b.p. 64-110°; 3.6 g
FractionII, b.p. 110-135°; 10.8 g
Residue 3 g

Distillation of Fraction II yielded 8 g (36.5%) of a substance boiling at 120° (1 mm) and having n_D^{20} 1.4656; d_4^{20} 1.0420.

Found %: P 19.42; 19.34
$C_9H_{23}P_2NSO_5$. Calculated %: P 19.43

The substance is a mobile yellow liquid, only slightly soluble in water, but readily soluble in organic solvents.

6. Tetraethyl Ester of Bis[phosphoric acid] Ethylamide $(C_2H_5O)_2P(O)-N(C_2H_5)-P(O)[N(CH_3)_2]_2$

The conditions were as in the preceding experiments. The substances taken were diethyl N-ethylphosphoramidate (15 g), sodium (1.9 g), and diethyl phosphorochloridate (14.3 g). The yield of crude product, a dark-yellow liquid, was 22.6 g (86%). Two distillations yielded 13.7 g (52.15%) of a substance boiling at 123-124° (1 mm).

Found %: P 19.94; 19.96

$C_{10}H_{25}P_2NO_5$. Calculated %: P 19.56

The substance is a very mobile, colorless liquid, readily soluble in water.

7. Diethyl Ester of the Mixed Ethylamide of Phosphoric and N,N,N',N'-Tetramethylphosphorodiamidic Acids $(C_2H_5O)_2P(O)-N(C_2H_5)-P(O)[N(CH_3)_2]_2$

The substance taken for reaction were diethyl N-ethylphosphoramidate (15 g), sodium (1.9 g), and N,N,N',N'-tetramethylphosphorodiamidic chloride (14.12 g). The yield of crude product was 23.1 g (83.5%). Two distillations yielded 13.3 g (50.9%) of a fraction boiling at 138-139° (2 mm) and having n_D^{20} 1.4609; d_4^{20} 1.1345.

Found %: P 19.94; 20.04

$C_{10}H_{27}P_2N_3O_4$. Calculated %: P 19.68

The substance is a fairly mobile, colorless liquid, readily soluble in water and ether.

8. Tetraethyl Ester of Bis[phosphoric acid]Anilide $(C_2H_5O)_2P(O)-N(C_6H_5)-P(O)(OC_2H_5)_2$

Diethyl phosphorochloridate (15.1 g) was added at room temperature to a benzene solution of diethyl N-phenyl-N-sodiophosphoramidate prepared from 20 g of the amide and 2 g of sodium. Reaction was completed by heating the flask in a water bath for one hour. The benzene solution of the product was treated with water to remove sodium chloride and then dried with calcium chloride. The solvent was removed under reduced pressure, and the residue was a fairly mobile, dark-red liquid. The liquid did not crystallize when allowed to stand, and it decomposed when distilled.

SUMMARY

1. A series of organophosphorus compounds of formula $(C_2H_5O)_2P(O)-N(R)-PR'_2$ (R is CH_3, C_2H_5, C_6H_5; R' is C_2H_5O, $N(CH_3)_2$) has been prepared and some of the properties of the compounds have been described.

2. Tests on corn weevils show that compounds of this type are insecticides.

LITERATURE CITED

[1] G. Shrader. Prog. Chem., 22, 6, 712-761 (1953); N. N. Melnikov, Prog. Chem., 22, 3, 253-278 (1953).

Received January 16 1954

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DETERMINATION OF THE INDIVIDUAL HYDROCARBON COMPOSITION OF GASOLINES BY THE COMBINATION METHOD

COMMUNICATION 6. KARACHUKHURSK GASOLINE

B. A. Kazansky, G. S. Landsberg, A. F. Plate, A. L. Liberman
E. A. Mikhailova, Kh. E. Sterin, T. F. Bulanova,
G. A. Tarasova, and V. T. Aleksanyan

In the present communication we give the results of an investigation of the individual hydrocarbon composition of a gasoline having an upper boiling limit of 150° obtained from low-sulfur lower-level Karachukhursk petroleum. The investigation was carried out by the previously described combination method [1], which we have applied to the investigation of two gasolines from Kazanbulak petroleums [2], two Surakhan gasolines [3], a gasoline derived from Tuimazin petroleum [4], and a gasoline from Embensk petroleum [5]. The gasoline used in the present work, like the Surakhan gasolines, was not separated from the petroleum by distillation in the laboratory, but was obtained in the prepared state from the V. V. Kuibyshev Azerbaidzhan Research Institute for the Petroleum-refining Industry.

As a result of the investigation the composition of the Karachukhursk gasoline was accounted for quantitatively to the extent of 85.4%. Altogether, 64 hydrocarbons were found in the gasoline, and the contents of these were determined quantitatively. Their distribution by classes is shown in Table 1.

TABLE 1

Distribution by Classes of the Hydrocarbons Found

Class of hydrocarbons	Number of hydrocarbons in the gasoline
Paraffins	32
Cyclopentanes	12
Cyclohexanes	14
Aromatics	6
	64

In the further discussion the gasoline under investigation will be denoted by TsCh-1. The same symbols will be used for the fractions as were used in the previous papers [1-5].

The contents of all individual hydrocarbons found in the gasoline have been calculated as percent by weight of the whole gasoline, i.e. all that distils up to 150°, and these figures are given in Table 2. In the same table we give the overall quantitative balance sheet for the investigation, and also the group composition of the Karachukhursk gasoline, in which normal and branched paraffins, and also cyclopentane and cyclohexane hydrocarbons, are considered separately.

As will be seen from Table 2, the gasoline from lower-level Karachukhursk petroleum contains 35.5% of paraffins and 33.5% of naphthenes. The paraffin-naphthene part of TsCh-1 contains 51.5% of paraffins and 48.5% of naphthenes. The naphthene part consists of 30.7% of cyclopentanes and 69.3% of cyclohexanes, i.e. the ratio of the amounts of cyclopentanes and cyclohexanes is 0.44. The proportions of the normal paraffins are (the total amount of normal paraffins being 100%) butane 1%, pentane 8.4%, hexane 22.7%, heptane 30.4%, and octane 37.5%; nonane is present, but has not been determined quantitatively. Of the C_6 branched paraffins present, 91.5% consists of methylpentanes, and only 8.5% of dimethylbutanes.

In the gasoline from lower-level Karachukhursk petroleum, as in the gasolines that we have investigated previously, there is very little cyclopentane. Of the cyclopentane hydrocarbons present, 3.8% is cyclopentane, 11.7% is methylcyclopentane, 46.7% consists of ethylcyclopentane and dimethylcyclopentanes, and 23.4% of C_9 cyclopentane hydrocarbons. The cyclohexane group consists mainly of C_7 and C_8 hydrocarbons. Of the cyclohexane hydrocarbons present, 10.6% is cyclohexane, 34.3% is methylcyclohexane, 37.6% consists of C_8 hydrocarbons, and 17.5% of C_9 hydrocarbons.

As in most of the gasolines investigated previously, among the aromatic hydrocarbons there is a predominance of C_8 compounds, i.e. ethylbenzene and xylenes. Of the aromatic hydrocarbons present, 6.3% is benzene, 34.3% is toluene, and 59.4% is represented by the xylene fraction. In this fraction there is more m-xylene than any other component, for of the C_8 hydrocarbons present, 26% is ethylbenzene, 40% is m-xylene, 20% is o-xylene, and 14% is p-xylene.

TABLE 2

Individual Hydrocarbons found in the Gasoline TsCh-1

Hydrocarbon	Content (% by weight on TsCh-1)	Hydrocarbon	Content (% by weight on TsCh-1)
Paraffin hydrocarbons			
Butane	0.14	2-Methylheptane	2.10
Pentane	1.18	3-Methylheptane	3.37
2-Methylbutane	0.13	4-Methylheptane	0.64
Hexane	3.17	2,2-Dimethylhexane	0.36
2-Methylpentane	1.00	2,3-Dimethylhexane	0.40
3-Methylpentane	0.83	2,5-Dimethylhexane	0.74
2,2-Dimethylbutane	0.11	3-Ethylhexane	0.63
2,3-Dimethylbutane	0.06	Nonane	+
Heptane	4.26	2-Methyloctane	1.01
2-Methylhexane	1.47	3-Methyloctane	1.01
3-Methylhexane	1.17	4-Methyloctane	0.50
2,2-Dimethylpentane	0.20	2,3-Dimethylheptane	2.84
2,4-Dimethylpentane	0.49	2,5-Dimethylheptane	1.33
3,3-Dimethylpentane	0.20	2,2,4-Trimethylhexane	0.24
3-Ethylpentane	0.24	2,3,5-Trimethylhexane	0.24
Octane	5.24	2,4,4-Trimethylhexane	0.23
		Total	35.53
Cyclopentane hydrocarbons			
Cyclopentane	0.39	Isopropylcyclopentane	0.22
Methylcyclopentane	1.20	$1^c, 2^t, 3^c$-Trimethylcyclopentane	0.50
Ethylcyclopentane	1.35	$1^t, 2^c, 3^c$-Trimethylcyclopentane	0.49
1,1-Dimethylcyclopentane	0.62	$1^c, 2^t, 4^c$-Trimethylcyclopentane	0.76
cis-1,2-Dimethylcyclopentane	0.20	Other cyclopentane homologs	1.48
trans-1,2-Dimethylcyclopentane	1.38	Total	10.28
1,3-Dimethylcyclopentane	1.25		
Propylcyclopentane	0.44		
Cyclohexane hydrocarbons			
Cyclohexane	2.46	1-Ethyl-3-methylcyclohexane	0.81
Methylcyclohexane	7.99	1-Ethyl-4-methylcyclohexane	0.41
Ethylcyclohexane	4.24	1,1,3-Trimethylcyclohexane	1.62
1,1-Dimethylcyclohexane	0.40	1,2,3-Trimethylcyclohexane	0.13
1,2-Dimethylcyclohexane	1.55	1,2,4-Trimethylcyclohexane	0.27
1,3-Dimethylcyclohexane	1.69	Total	23.24
1,4-Dimethylcyclohexane	0.85		
Propylcyclohexane	0.41		
1-Ethyl-2-methylcyclohexane	0.41		
Aromatic hydrocarbons			
Benzene	1.03	o-Xylene	1.96
Toluene	5.62	m-Xylene	3.93
Ethylbenzene	2.46	p-Xylene	1.37
		Total	16.37

(Table continues on next page)

Accounted for (% on TsCh-1)	85.42
Not accounted for quantitatively	4.59
Residues remaining after fractionations	2.69
Losses*	7.30
Total (% on TsCh-1)	100.00

Group Composition of the Gasoline TsCh-1 % on gasoline)

Normal paraffins	13.99
Paraffins containing a tertiary carbon atom	20.20
Paraffins containing a quaternary carbon atom	1.34
Cyclopentanes	10.28
Cyclohexanes	23.24
Aromatics	16.37

* Including small amounts of sulfur compounds contained in the original gasoline.

EXPERIMENTAL *

The sample of gasoline (n_D^{20} 1.4219; d_4^{20} 0.7526; aniline point 43.7°; content of unsaturateds 1.3%; sulfur content 0.034% by weight) was regarded as a wide cut ShCh-1 and was fractionated through a 25-plate column. The results of the fractionation are given in Table 3 and Fig. 1. In this fractionation no gaseous part was obtained. The light and main fractions, taken together, formed the "whole gasoline" TsCh-1, amounting to 1637 g.

TABLE 3

Fraction	Boiling limits (°C at 760 mm)	Weight (g)	Content of fraction (% by weight)	
			in ShCh-1	in TsCh-1
Taken for distillation	–	1780	100.00	–
LCh-1 (light fraction)	23.8–55.5	36	2.02	2.20
ACh-1 (main fraction)	55.5–150.0	1601	89.94	97.80
Residue	above 150	119	6.69	–
Losses	–	24	1.35	–

Investigation of the Light Fraction. After removal of sulfur compounds by chromatographic adsorption (the losses amounted to 0.05% on TsCh-1), the light fraction LCh-1 was distilled through a 40-plate column. Fractions were taken, and the fractionation curve (Fig. 2) was determined at the same time. The amounts of the fractions obtained, and their properties, are given in Table 4.

TABLE 4

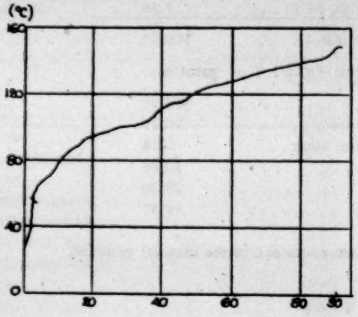
Results of the Fractionation of the Light Fraction LCh-1

Fraction No.	Boiling limits (°C at 760 mm)	Weight (g)	n_D^{20}	d_4^{20}	Content of fraction (% by weight)	
					in LCh-1	in TsCh-1
Taken for fractionation		34.1			100.00	2.14
	Butane (in coil)	2.2	–	–	6.45	0.14
I	27.7 – 32.0	2.1	1.3528	0.6163	6.16	0.13
II	32.0 – 42.0	18.75	1.3572	0.6244	54.98	1.18
	Residue	7.9			23.17	0.50
	Losses	3.15			9.24	0.20

As can be seen from Table 4, the constants of Fraction I correspond to those of 2-methylbutane (b.p. 27.85°; n_D^{20} 1.3537; d_4^{20} 0.6197), and the constants of Fraction II are close to those of pentane (b.p. 36.07°; n_D^{20} 1.3575; d_4^{20} 0.6262). The residue from the fractionation of LCh-1, after removal of fluorescent substances by chromatographic adsorption (when it had n_D^{20} 1.3887; d_4^{20} 0.7157), was investigated by the Raman spectrum method. The results are given in Table 5. In the present communication we publish frequencies and visually estimated intensities of the spectrum lines of the narrow fractions. The qualitative compositions of the fractions were established from these data.

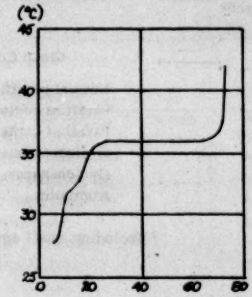
* Laboratory assistants T. V. Lapishina, K. G. Ryabova, and G. S. Taits took part in the experimental work.

Spectrum of residue: $\Delta\nu$ (cm^{-1})*: 325(1.b); 392(0); 445(3); 478(1); 505(0); 711(4); 731(1); 752(1.b); 785(1); 813 (4b); 866(0); 887(9b); 924(od); 936(1); 949(0); 960(0); 969(0); 983(0); 1017(2); 1028(6b); 1038(3); 1053(1); 1101(1); 1146(3b); 1173(2b); 1213(2bg); 1220(0); 1249(2b); 1274(0b); 1282(1); 1299(3b); 1309(1); 1339(1b); 1364(0).



% by volume

Fig. 1. Fractionation curve for the gasoline ShCh-1.



% by volume

Fig. 2. Fractionation curve for the light fraction LCh-1.

In order to make quantitative determinations, multiple photographs were taken of the spectra of the fractions and of the standard hydrocarbon, and some of the lines were measured and their intensities determined from the laws of photographic photometry.

Separation of the Aromatic Hydrocarbons from the Mixture of Paraffins and Naphthenes in the Main Fraction ACh-1. Aromatics were separated from the A fraction (n_D^{20} 1.4217; d_4^{20} 0.7481; aniline point 42.5°; sulfur content 0.03%; content of unsaturateds 1.2%) with the aid of chromatographic adsorption on silica gel. Table 6 gives the amounts of the fractions both the amounts actually isolated, and the corrected amounts, i.e. corrected for the amounts used for qualitative tests for aromatics and for refractive index determinations. This table shows the results of the separation; also, in Fig. 3 a curve is given for the variation in refractive index when 18 ml of Fraction A was passed through 30 g of silica gel.

The dearomatized fraction VCh-1 contained neither sulfur nor unsaturated hydrocarbons. The aromatic fraction, which contained sulfur, was again passed through the silica gel column. The fractions obtained had the following properties: BCh-1: n_D^{20} 1.4978; d_4^{20} 0.8666; aniline point 58.9°. VCh-1: n_D^{20} 1.4092; d_4^{20} 0.7348; aniline point 58.9°.

Investigation of the Aromatics BCh-1. The aromatic hydrocarbons (Fraction BCh-1) were fractionated through a 40-plate column into benzene, toluene, and xylene fractions, the fractionation curve (Fig. 4) being determined at the same time. In order to complete the distillation of the xylene fraction, pure decahydronaphthalene was added toward the end of the distillation.

We give below the Raman spectrum of the xylene fraction:

$\Delta\nu$ (cm^{-1}): 207(2); 231(4); 256(2); 279(3); 311(2); 457(3s); 486(1); 504(2); 515(4); 537(7s); 582(5s); 623(1); 644(1); 727(8s); 734(8s); 770(3); 788(0); 813(2); 830(5); 858(0); 1001(9); 1031(3); 1053(6); 1096(2d); 1158(4b); 1170(3b); 1205(6); 1222(6); 1250(7); 1263(2); 1310(0b); 1378(7).

The results of the fractionation of the aromatics BCh-1 and the properties of the fractions are given in Table 7.

As will be seen from the data in Table 7, according to their physical properties, Fraction I can be regarded as a benzene fraction, and Fraction II as a toluene fraction; we may assume that the amounts of these fractions correspond to the contents of benzene and toluene in the gasoline. The results of the optical analysis of Fraction III are given in Table 8.

Dehydrogenation of Cyclohexane Hydrocarbons. With the object of converting the cyclohexane hydrocarbons into aromatics, the paraffin-naphthene fraction VCh-1 was subjected to catalytic dehydrogenation, for which purpose it was passed over an iron-platinum catalyst at 300° at a space velocity of 0.9-1.0 liter per liter of catalyst per hour (at the same temperature and at a space velocity of 0.94, the catalyst dehydrogenated cyclohexane

* Symbols in parentheses: the numbers are intensities on a ten-grade scale; the letters have the following meanings - b - broad line, s sharp line, d - doublet, g -background.

to the extent of 90%). The dehydrogenation of VCh-1 was complete in one passage. From 651.3 g of VCh-1, 611.8 g (93.94% on VCh-1) of catalyzate GCh-1 was obtained (611.3 g actually collected and 0.5 g used for tests). The amount of GCh-1 calculated on TsCh-1 was 75.01%.

TABLE 5

Results of the Optical Investigation of the Residue from the Light Fraction LCh-1

Hydrocarbons found	Content (% by weight)	
	in residue	in whole gasoline TsCh-1
Residue.	100	0.50
Cyclopentane.	55	0.28
2-Methylpentane.	10	0.05
3-Methylpentane.	20	0.10
2,2-Dimethylbutane.	10	0.05
2,3-Dimethylbutane.	5	0.02

The losses (39.5 g i.e. 6.06% on VCh-1, or 4.84% on TsCh-1) included the hydrogen formed in the dehydrogenation of the cyclohexane hydrocarbons, the amount of which was not determined. After the experiment the catalyst still retained its activity, as indicated by its behavior in the dehydrogenation of cyclohexane.

The physical properties of the original fraction VCh-1 and of the dehydrogenation catalyzate GCh-1 were:

	n_D^{20}	d_4^{20}	Aniline point (°C)
VCh-1	1.4092	0.7348	58.9
GCh-1	1.4248	0.7543	39.5

The catalyzate GCh-1 contained a small amount of unsaturated hydrocarbons (1.4%).

Separation of the Catalyzate GCh-1 into Aromatic Hydrocarbons and a Mixture of Paraffins and Cyclopentanes. The catalyzate GCh-1 was separated chromatographically into an aromatic fraction DCh-1 and a paraffin-cyclopentane fraction ECh-1. The results of the separation of the catalyzate GCh-1 are given in Table 9.

The fractions separated, DCh-1 and ECh-1 (after removal of pentane by distillation) had the following properties:

	n_D^{20}	d_4^{20}	Aniline point
Ch-1	1.4970	0.8666	–
ECh-1	1.4029	0.7195	65.5

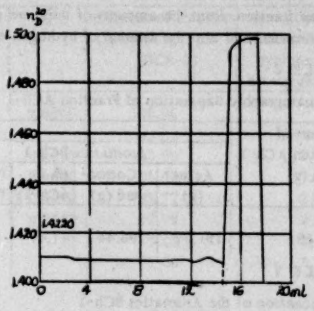


Fig. 3. Curve for the variation in refractive index during chromatographic separation of Fraction ACh-1.

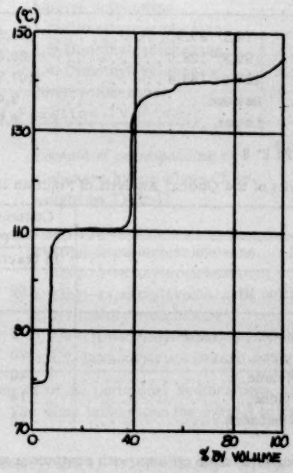


Fig. 4. Fractionation curve for the aromatic fraction BCh-1.

Investigation of the Aromatics DCh-1. Fraction DCh-1 was fractionated through a 40-plate column (similarly to the aromatics BCh-1). The results of the fractionation, the properties of separate fractions, and the results of the optical analysis, calculated back to the corresponding hydrocarbons, are given in Fig. 5 and Table 10. We give below the Raman spectra of Fractions III and IV.

Frac. III. $\Delta\nu$ (cm^{-1}): 232(4b); 257(3b); 279(2b); 314(4b); 388(0d); 459(4s); 487(2d); 506(3s); 518(4s); 537(6s); 556(0s); 582(5s); 624(4); 646(2); 726(8s); 735(8s); 771(4); 788(3s); 813(2); 830(6); 970(2d); 986(1); 1003(10); 1032(6); 1053(7); 1097(1); 1157(3); 1181(1d); 1205(6); 1224(4); 1251(5s); 1267(1s); 1287(1d); 1322(1b); 1380(9);

Frac. IV. $\Delta\nu$ (cm^{-1}): 212(4b); 225(4b); 256(1); 282(1); 318(3); 420(0); 440(0); 473(2); 509(2d); 530(2); 554(3); 580(4); 620(1); 643(1); 658(2); 719(6s); 735(6s); 746(5s); 807(2d); 820(2d); 923(1); 972(1); 988(1); 1003(7); 1029(2);

1054(5); 1059(1); 1095(1); 1159(1); 1185(0); 1202(1); 1223(2); 1247(4); 1278(0); 1324(1b); 1382(6).

The data in Table 10 show also that Fraction I can be regarded as a benzene fraction, and Fraction II as a toluene fraction; from the amounts of these we can calculate the corresponding amounts of cyclohexane and methylcyclohexane, and also the amount of hydrogen that separated in the dehydrogenation (1.25% on TsCh-1).

TABLE 6

Chromatographic Separation of Fraction ACh-1

Amount of Fraction ACh-1 taken (g)	Results of Separation										
	Aromatics BCh-1				Paraffins and naphthenes VCh-1				Losses		
	Actual (g)	Corrected (g)	(% in ACh-1)	(% in TsCh-1)	Actual (g)	Corrected (g)	(% in ACh-1)	(% in TsCh-1)	(g)	(% in ACh-1)	(% in TsCh-1)
1135.58	191.77	198.44	17.47	17.09	925.34	327.16	81.65	79.85	9.98	0.88	0.86

TABLE 7

Fractionation of the Aromatics BCh-1

Fraction No.	Boiling limits (°C at 760 mm)	Weight (g)	n_D^{20}	d_4^{20}	Content of fraction (% by weight)	
					in BCh-1	in TsCh-1
Taken for fractionation		187.4	1.4978	0.8666	100.00	17.09
I	74.1–99.9	11.3	1.4970	0.8695	6.03	1.03
II	99.9–128.0	60.5	1.4937	0.8664	32.28	5.52
III	128.0–143.4	107.7	1.4991	0.8680	57.47	9.82
	Residue	2.0			1.07	0.18
	Losses	5.9			3.15	0.54

TABLE 8

Results of the Optical Analysis of Fraction III

	Content of hydrocarbon (% by weight)	
	in Fraction III	in TsCh-1
Fraction III	100	9.82
Toluene	1	0.10
o-Xylene	20	1.96
m-Xylene	40	3.93
p-Xylene	14	1.37
Ethylbenzene	25	2.46

Investigation of Paraffin-Cyclopentane Fraction ECh-1. A portion (100 ml) of the paraffin-cyclopentane fraction was fractionated through a 50-plate column in order to determine the fractionation curve. The distillation was carried out at a reflux ratio of 45–50 with continuous separation of distillate. The fractionation curve is given in Fig. 6. The vertical lines indicate the limits between which narrow fractions were taken in the subsequent fractionation; the selection of these limits was determined by the form of the fractionation curve and by the boiling points of individual hydrocarbons.

When the fractionation curve had been determined, 300 ml of Fraction ECh-1 was fractionated through the same column with continuous separation of distillate and at a reflux ratio of 40–45. Altogether, 15 narrow fractions were taken. The results of the fractionation of the paraffin-cyclopentane fraction into narrow fractions and the properties of these fractions are given in Table 11. The Raman spectra of these fractions are given below.

TABLE 9

Chromatographic Separation of the Catalyzate GCh-1

Catalyzate GCh-1 taken (g)	Results of separation										
	Aromatics DCh-1				Paraffin-cyclopentane fraction ECh-1				Losses		
	Actual (g)	Corrected (g)	(% in GCh-1)	(% in TsCh-1)	Actual (g)	Corrected (g)	(% in GCh-1)	(% in TsCh-1)	(g)	(% in GCh-1)	(% in TsCh-1)
588.22	152.59	158.06	26.87	20.16	421.10	421.73	71.70	53.78	8.43	1.43	1.07

The results of the quantitative optical analysis, which was in close accord with the physical properties of the narrow fractions, are given in Table 12.

TABLE 10

Fractionation of the Aromatics DCh-1

Fraction No.	Boiling limits (°C at 760 mm)	Weight (g)	n_D^{20}	d_4^{20}	Content of fraction (% by weight on DCh-1)	Content of fraction of corresponding cyclohexanes (% by weight on TsCh-1)
Taken for fractionation		43.0	1.4970	0.8666	100.00	
I	78.0–100.3	4.7	1.4958	0.8695	10.93	2.37
II	100.3–128.4	15.1	1.4956	0.8640	35.12	7.54
III	128.4–147.4	17.1	1.4978	0.8672	39.77	8.48
IV	147.4–167.3	5.5	1.4996	0.8701	12.79	2.71
	Residue	0.0			0.00	0.00
	Losses	0.6			1.39	0.30

Results of the Optical Analysis of Fraction III of DCh-1

Content of aromatic hydrocarbons (% by weight on Fraction III)		Content of corresponding cyclohexane hydrocarbons (% by weight on TsCh-1)	
Toluene	5	Methylcyclohexane	0.42
o-Xylene	15	1,2-Dimethylcyclohexane	1.28
m-Xylene	20	1,3-Dimethylcyclohexane	1.69
p-Xylene	10	1,4-Dimethylcyclohexane	0.85
Ethylbenzene	50	Ethylcyclohexane	4.24

Results of the Optical Analysis of Fraction IV of DCh-1

Content of aromatic hydrocarbons (% by weight on Fraction IV)		Content of corresponding cyclohexane hydrocarbons (% by weight on TsCh-1)	
Propylbenzene	15	Propylcyclohexane	0.41
1-Ethyl-2-methylbenzene	15	1-Ethyl-2-methylcyclohexane	0.41
1-Ethyl-3-methylbenzene	30	1-Ethyl-3-methylcyclohexane	0.81
1-Ethyl-4-methylbenzene	15	1-Ethyl-4-methylcyclohexane	0.41
o-Xylene	10	1,2-Dimethylcyclohexane	0.27
1,2,4-Trimethylbenzene	10	1,2,4-Trimethylcyclohexane	0.27
1,2,3-Trimethylbenzene	5	1,2,3-Trimethylcyclohexane	0.13

All of the data obtained in the course of the investigation for the contents of the individual hydrocarbons, expressed as percent by weight on the whole gasoline TsCh-1, are given in Table 2. The same table shows the overall balance sheet for the investigation.

$\Delta\nu$ (cm^{-1}): Frac. I: 262(0); 326(3b); 370(1); 391(1); 446(6s); 479(1); 546(0); 586(0); 711(1); 731(4); 748(3b); 763(1); 781(0); 794(1); 812(8); 863(0b); 887(6b); 922(0); 937(1b); 956(4); 981(2b); 1015(2b); 1036(7); 1071(1b); 1145(5b); 1167(5b); 1196(0); 1245(0); 1277(1b); 1299(5b); 1343(3b); 1355(2b).

Frac. II: 306(1b); 314(3b); 326(1b); 340(1); 372(2); 403(1); 533(3); 810(3b); 825(4b); 838(3b); 846(1); 870(2); 891(6b); 979(2); 1010(2); 1039(3); 1065(0); 1083(4b); 1135(2b); 1162(0); 1191(1b); 1278(2b); 1302(5b); 1353(1b).

Frac. III: 253(0); 306(2); 324(1); 349(1); 372(0); 410(0); 433(2b); 468(0); 495(1); 530(1b); 559(1); 692(2); 767(0); 784(1); 801(5s); 807(5); 823(2); 846(1); 890(5); 915(0); 922(2); 938(2); 956(3); 984(0); 1006(0); 1027(4); 1042(1); 1057(1); 1080(3); 1098(3); 1146(5b); 1161(4b); 1172(4b); 1191(3b); 1207(2); 1247(1); 1264(1); 1301(4b); 1317(2); 1329(3); 1346(3).

Frac. IV: 263(0); 283(0); 312(2); 322(1); 347(1); 377(1b); 397(0); 416(0); 432(3b); 446(2); 496(4s); 513(1b); 526(0); 557(0); 718(1); 730(1); 768(4); 784(2); 800(3); 824(5); 864(1); 877(1); 897(6); 930(0); 945(0); 957(3); 983(4); 989(5); 1018(1); 1030(3); 1044(4b); 1064(0); 1074(2); 1080(6b); 1086(2); 1101(3); 1146(5b); 1173(4b); 1187(0); 1226(0); 1250(0); 1285(1); 1301(7b); 1340(6b); 1348(2); 1355(4b).

Frac. V: 260(0); 285(0); 312(4); 357(0); 398(2b); 439(1); 469(1); 499(3); 527(0); 735(2b); 767(4b); 801(2); 833(4b); 850(3b); 867(1); 899(6b); 932(2); 956(2); 980(1); 1023(4b); 1039(5b); 1082(7b); 1104(1); 1139(7b); 1167(1); 1202(1); 1275(1); 1302(8); 1338(2); 1356(0).

Frac. VI: 283(0); 312(5); 331(0); 358(0); 394(2); 402(2); 455(0); 501(2); 585(0); 603(0); 679(0); 694(0); 727(0); 738(0); 761(3); 774(3); 824(2); 835(5b); 853(4b); 888(4); 902(6); 933(2); 949(2g); 960(2g); 981(1); 1024(2); 1043(3); 1064(2); 1079(5); 1105(1); 1136(5); 1162(2); 1195(2); 1236(1); 1267(2); 1281(1); 1303(8b); 1346(0); 1386(2b).

Frac. VII: 263(0); 272(0); 287(0); 309(2); 339(1); 366(0); 396(3b); 408(2); 415(3b); 425(1); 444(1b); 482(1); 494(4); 521(2); 719(0); 746(2); 769(5); 795(1); 802(2g); 814(1); 838(3); 852(1); 874(2); 892(4); 902(1g); 927(2); 937(2); 946(2); 958(2); 968(1); 992(1); 1014(2); 1024(3); 1043(3); 1056(2b); 1069(2); 1083(2); 1088(2); 1103(1); 1135(2); 1146(1); 1162(2); 1190(2); 1203(0); 1234(0); 1250(0); 1267(1); 1295(4); 1305(4); 1318(3); 1336(2); 1354(2).

Frac. VIII: 259(1b); 266(0); 287(1); 317(2); 330(0); 405(1); 418(0); 428(0); 443(1); 460(0); 493(4); 521(3); 552(0); 598(0); 607(1); 616(0); 671(0); 686(0); 717(0); 723(0); 733(0); 756(1); 768(5); 780(1); 816(4); 834(2); 858(0); 877(2); 892(3); 909(1g); 946(2g); 956(4b); 991(0); 1008(0); 1025(1); 1042(3); 1058(0); 1080(1b); 1100(2b); 1143(4b); 1157(4b); 1172(2); 1191(2b); 1202(1); 1246(0); 1274(0); 1305(4); 1324(1); 1337(3); 1352(2).

Frac. IX: 247(0); 259(1); 269(1); 278(1); 288(3); 298(2); 314(2); 322(2); 328(0); 350(1b); 370(1g); 384(1g); 407(2g); 417(0); 426(2g); 432(1); 440(1); 448(1); 489(1); 513(1); 548(0); 560(0); 573(0); 676(0); 703(5s); 729(2); 746(2); 762(4b); 795(0); 814(3b); 822(2); 830(1); 839(1); 858(0); 869(2); 877(1); 892(3); 904(2); 934(1); 944(0); 956(3b); 970(2b); 980(1); 1008(2); 1029(1); 1043(3); 1060(0); 1077(4); 1099(1); 1110(1); 1126(0); 1143(5); 1154(3b); 1164(1); 1175(1); 1190(2b); 1244(2b); 1267(1b); 1301(5b); 1338(3); 1360(2b).

Frac. X: 246(0); 260(0); 282(3); 296(1); 316(1); 323(0); 372(0); 401(0); 416(1); 426(1); 448(1); 460(1b); 492(1); 513(0); 525(1); 556(1); 586(0); 597(0); 645(0); 704(5); 730(0); 747(0); 759(2); 768(1); 795(0); 806(2); 819(2); 828(1); 841(0); 851(0); 860(0); 875(2); 894(4); 907(1); 917(0); 938(1b); 964(3); 972(2); 985(1); 1028(3b); 1039(3b); 1048(1); 1056(1); 1066(1); 1078(3); 1088(2); 1134(2); 1145(0); 1161(1); 1171(0); 1193(2); 1223(0); 1242(1); 1257(0); 1264(1); 1282(1); 1302(5b); 1343(1); 1351(1).

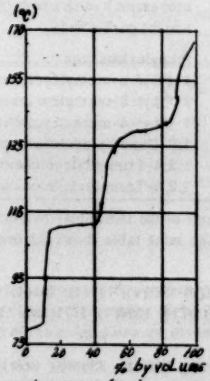


Fig. 5. Fractionation curve for the aromatics DCh-1

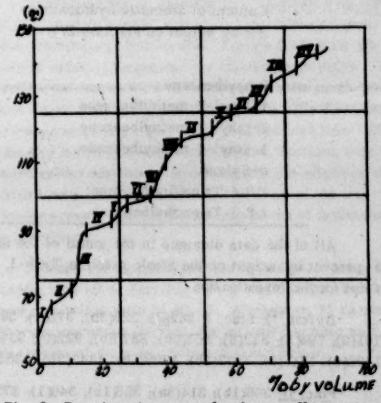


Fig. 6. Fractionation curve for the paraffin-cyclopentane fraction. ECh-1.

Frac. XI: 245(0); 260(0); 282(6); 295(1b); 306(0); 318(0); 334(0); 352(0); 372(1b); 393(0); 403(0); 414(1); 427(2); 456(1); 493(1); 511(0); 521(0); 529(0); 544(0); 562(0); 573(0); 590(0); 625(0); 668(0); 690(0); 705(1); 719(0); 730(1); 766(2); 790(2); 806(2); 817(3); 841(3); 860(4); 876(4); 895(5); 920(0); 932(0); 956(2); 967(2); 982(0); 1003(0); 1026(3); 1043(3); 1061(5s); 1082(7s); 1109(0); 1135(5s); 1153(1); 1164(2); 1198(2); 1222(0); 1246(0); 1254(0); 1273(1); 1303(8); 1341(1);

TABLE 11

Results of the Fractionation of the Paraffin-Cyclopentane Fraction ECh-1

Fraction No.	Boiling limits (°C at 760 mm)	Weight (g)	Content of fraction (% by weight)		n_D^{20}	d_4^{20}	Aniline point (°C)
			in ECh-1	in TsCh-1			
Taken for fractionation		218.5	100.00	53.76	1.4029	0.7195	–
I	48.3–67.0	8.5	3.89	2.09	1.3753	0.6622	68.2
II	67.0–72.0	16.5	7.55	4.06	1.3896	0.6972	53.4
III	72.0–90.0	8.0	3.66	1.97	1.3980	0.7142	57.6
IV	90.0–92.5	19.0	8.70	4.68	1.3977	0.7129	60.5
V	92.5–98.0	6.4	2.93	1.58	1.3936	0.7011	63.8
VI	98.0–99.5	16.2	7.41	3.99	1.3902	0.6907	67.1
VII	99.5–110.0	9.8	4.44	2.39	1.4068	0.7335	58.6
VIII	110.0–117.0	10.8	4.94	2.66	1.4047	0.7250	66.3
IX	117.0–120.0	19.7	9.02	4.85	1.4033	0.7191	67.6
X	120.0–124.5	12.9	5.90	3.17	1.4053	0.7245	65.5
XI	124.5–126.5	20.0	9.15	4.92	1.4002	0.7113	69.6
XII	126.5–133.5	7.2	3.30	1.77	1.4100	0.7350	66.2
XIII	133.5–138.0	18.0	8.24	4.43	1.4182	0.7537	64.3
XIV	138.0–143.0	20.5	9.38	5.04	1.4123	0.7377	69.6
XV	143.0–148.5	12.1	5.54	2.98	1.4150	0.7428	67.5
	Residue	10.2	4.67	2.51			
	Losses	2.8	1.28	0.69			

Frac. XII: 249(0); 264(0); 282(3); 300(0); 321(1b); 332(1); 342(1); 362(1); 401(0); 420(1); 437(0); 455(1); 469(1); 480(1); 496(1); 534(0); 555(1s); 645(0); 682(0); 708(1); 726(3s); 743(2); 762(3b); 790(2); 815(4bg); 820(2); 828(1); 840(3g); 862(2g); 878(2g); 896(6s); 927(1bg); 956(3b); 973(2b); 1001(0); 1016(1); 1031(3g); 1043(2); 1058(3g); 1085(4b); 1093(2b); 1107(2); 1130(1); 1141(b); 1166(5b); 1192(4); 1216(1); 1252(2); 1277(0b); 1303(8); 1323(1); 1341(2b); 1356(1); 1394(1b).

Frac. XIII: 250(1b); 263(0); 301(0); 324(3); 345(0g); 368(0b); 398(0); 422(2g); 436(2g); 465(3); 499(1); 519(1); 556(6); 629(0); 669(1); 726(7s); 749(0b); 766(5); 786(1b); 796(3); 806(3); 814(3); 837(3b); 850(1); 869(1b) 896(3); 905(2); 935(4); 954(4); 974(4b); 982(4b); 1009(0); 1017(1); 1032(1b); 1097(3b); 1145(4b); 1168(4b); 1190(5); 1220(2); 1247(3); 1281(3b); 1295(5b); 1306(4b); 1320(2); 1341(5b); 1355(3b); 1381(2b).

Frac. XIV: 257(1b); 286(1b); 297(0); 310(0); 324(0); 344(0); 379(0); 398(0); 429(1b); 461(1b); 511(1); 555(1); 576(1); 591(0); 619(1); 707(1); 726(3g); 759(3g); 769(3g); 797(1dg); 813(2); 822(2); 842(1dg); 857(1); 874(3bg); 892(4bg); 918(2); 927(2b); 938(2b); 954(3dg); 977(1dg); 1001(1dg); 1022(2); 1040(4 b. polarized); 1057(5 b. polarized); 1079(5 polarized); 1104(1b); 1140(6b); 1160(6b); 1191(3d); 1248(1d); 1276(1d); 1301(7b); 1344(4b); 1355(2b); 1386(2b).

Frac. XV: 250(2); 266(2); 283(2); 318(0); 342(0); 354(0); 382(0); 407(0); 415(0); 434(1); 454(0); 512(2b); 527(1g); 540(1g); 560(1g); 583(1g); 599(1b); 625(0); 648(0); 679(4); 712(0); 728(3); 745(2g); 766(1g); 790(1g); 815(4bg); 822(2); 834(4bg); 846(2b); 871(4); 892(5b); 909(1b); 920(0); 934(1); 953(2g); 970(2g); 980(1g); 1003(0b); 1014(1b); 1043(3b); 1060(2g); 1082(6b); 1137(6b); 1147(3); 1160(3b); 1189(0); 1201(1); 1242(1); 1273(1b); 1303(7b); 1346(3b); 1382(2b).

The results of the quantitative optical analysis, which was in close accord with the physical properties of the narrow fractions, are given in Table 12. All of the data obtained in the course of the investigation for the contents of the individual hydrocarbons, expressed as per cent by weight on the whole gasoline TsCh–1, are given in Table 2. The same table shows the overall balance sheet for the investigation.

SUMMARY

1. By means of the combination method of investigating the individual hydrocarbon compositions of straight-run gasolines, an analysis has been made of a gasoline having an upper boiling limit of 150° derived from lower-level Karachukhursk petroleum.

2. The individual hydrocarbon composition of the Karachukhursk gasoline has been accounted for quantitatively to the extent of 85.4% (by weight on the whole gasoline). The total losses in analysis were 7.30%, the residues in the distillation flasks amounted to 2.69%, and the composition of 4.59% of the gasoline remained undetermined. Altogether, 63 hydrocarbons have been determined quantitatively.

TABLE 12

Results of the Optical Investigation of Narrow Fractions of the Paraffin-Cyclopentane Fraction ECh-1

Hydrocarbons found optically	Content of hydrocarbon (% by weight)	
	in fraction	in TsCh-1
Fraction I		
Cyclopentane	5	0.10
2,2-Dimethylbutane	3	0.06
2,3-Dimethylbutane	2	0.04
2-Methylpentane	45	0.95
3-Methylpentane	35	0.73
Hexane	10	0.21
Fraction II		
Hexane	73	2.96
Methylcyclopentane	27	1.10
Fraction III		
Methylcyclopentane	5	0.10
2,2-Dimethylpentane	10	0.20
2,4-Dimethylpentane	25	0.49
Cyclohexane	5	0.09
3,3-Dimethylpentane	10	0.20
1,1-Dimethylcyclopentane	20	0.39
2-Methylhexane	15	0.30
trans-1,2-Dimethylcyclopentane	10	0.20
Fraction IV		
1,1-Dimethylcyclopentane	5	0.23
2-Methylhexane	25	1.17
1,3-Dimethylcyclopentane	25	1.17
3-Methylhexane	25	1.17
trans-1,2-Dimethylcyclopentane	20	0.94
Fraction V*		
1,3-Dimethylcyclopentane	5	0.08
trans-1,2-Dimethylcyclopentane	15	0.24
3-Ethylpentane	15	0.24
Heptane	60	0.95
Fraction VI*		
Heptane	80	3.19
cis-1,2-Dimethylcyclopentane	5	0.20
Ethylcyclopentane	10	0.40

Hydrocarbons found optically	Content of hydrocarbon (% by weight)	
	in the fraction	in TsCh-1
Fraction VII		
Heptane	5	0.12
Methylcyclohexane	1–2	0.03
Ethylcyclopentane	40	0.95
2,2-Dimethylhexane	15	0.36
$1^c,2^t,4^c$-Trimethylcyclopentane	10	0.23
2,5-Dimethylhexane	20	0.47
$1^c,2^t,3^c$-Trimethylcyclopentane	10	0.23
Fraction VIII		
$1^c,2^t,4^c$-Trimethylcyclopentane	20	0.53
2,5-Dimethylhexane	10	0.27
$1^c,2^t,3^c$-Trimethylcyclopentane	10	0.27
2,3-Dimethylhexane	15	0.40
2-Methylhexane	25	0.65
4-Methylhexane	10	0.27
3-Ethylhexane	10	0.27
Fraction IX		
2-Methylheptane	30	1.45
4-Methylheptane	15	0.73
3-Ethylhexane		
$1^t,2^c,3^c$-Trimethylcyclopentane	10	0.49
3-Methylheptane	40	1.94
1,1-Dimethylcyclohexane	5	0.24
Fraction X*		
3-Methylheptane	45	1.43
1,1-Dimethylcyclohexane	5	0.16
Octane	40	1.27
Fraction XI		
Octane	70	3.44
Cyclopentane homologs**	30	1.48

* Some lines have not been interpreted.

** It was not found possible to establish the composition of the cyclopentane homologs more exactly.

TABLE 12 (continued)

Hydrocarbons found optically	Content of hydrocarbon (% by weight)		Hydrocarbons found optically	Content of hydrocarbon (% by weight)	
	in the fraction	in TsCh-1		in the fraction	in TsCh-1
Fraction XII*			Fraction XIV*		
Octane	30	0,53	1,1,3-Trimethylcyclohexane	10	0,51
Isopropylcyclopentane, Propylcyclopentane	25	0,44	2,3-Dimethylheptane	30	1,51
2,2,4-Trimethylhexane, 2,3,5-Trimethylhexane, 2,4,4-Trimethylhexane	40	0,71	4-Methyloctane	10	0,50
			2-Methyloctane	20	1,01
			3-Methyloctane	20	1,01
Fraction XIII*			Fraction XV***		
Propylcyclopentane	5	0,22	4-Methyloctane, 2-Methyloctane, 3-Methyloctane, Nonane		
2,5-Dimethylheptane, 2,3-Dimethylheptane	60	2,66			
1,1,3-Trimethylcyclohexane	25	1,11			

* Some lines have not been interpreted

*** Many of the lines have not been interpreted. The components could not be accounted for quantitatively owing to the diffuse character of the lines.

SUMMARY (continued)

3. There is a considerable amount of aromatic hydrocarbons in the gasoline derived from lower-level Karachukhursk petroleum (more than in any of the gasolines investigated previously by this method [2-4]), namely 16.37%. There are approximately equal amounts of paraffin and naphthene hydrocarbons in the gasoline. Of the total amount of paraffin hydrocarbons, 40% consists of normal paraffins. The ratio of the amounts of cyclopentane and cyclohexane hydrocarbons is 0.44.

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Received December 19, 1953

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* See Consultants Bureau English translation, page 215.
** See Consultants Bureau English translation, page 225.
*** See Consultants Bureau English translation, page 387.
**** See Consultants Bureau English translation, page 747.

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HIGH-TEMPERATURE REACTIONS OF HEPTANE IN A CONTINUOUS-FLOW SYSTEM IN PRESENCE OF METALS OF THE PALLADIUM GROUP AND OF HYDROGEN AT HIGH PRESSURE

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The reactions of heptane in presence of hydrogen at high pressure have been studied in presence of platinum and nickel catalysts. Haensel and Donaldson [1], for example, investigated the reactions of heptane at 459° in presence of a platinum catalyst and hydrogen at a pressure of 35 atm. They found that, under these conditions, heptane yielded a complex mixture of paraffins, mainly of branched structure. Also, toluene in an amount corresponding to about 2% of the original heptane was found in the reaction products, and about 12.5% of the heptane was recovered unchanged.

The reactions of heptane at 460° in presence of platinized alumina and hydrogen at 20 atm in a flow system were investigated by Shuikin, Berdnikova, and Novikov [2]. These authors found that, apart from 12.2% of unchanged heptane, the catalyzate contained C_5-C_7 branched paraffins. In addition to the isomerization and cleavage reactions of the original hydrocarbon, the formation of a considerable amount (18%) of aromatic hydrocarbons was observed, and these included not only toluene, but also benzene, xylenes, and higher benzene homologs, which were not investigated in detail.

Ciapetta and Hunter [3] have recently investigated the reactions of heptane at 288-420° in presence of nickel on an aluminosilicate carrier and of hydrogen at 24.8 atm. At 353° the amount of C_7 branched hydrocarbons attained 67.2%, and this included 3-methylhexane, 2-methylhexane, and 2,4-dimethylpentane. Hydrocarbons of lower molecular weight were also formed.

The data in these papers show that platinum and nickel, depending on the nature of the carrier and the experimental conditions, are able to promote a variety of reactions of heptane. The present investigation forms a continuation of our study [4] of the specific features of the behavior of carrier-supported metal catalysts of low active-metal content in the hydrogenation and dehydrogenation reactions of hydrocarbons. We have now studied the behavior of heptane in presence of Ru, Rh, Pd, and Pt deposited on silica gel. It should be noted that the reactions of paraffins in presence of Ru and Rh catalysts have not been investigated previously.

Our experiments have shown that, at a high temperature and a high pressure of hydrogen in a continuous-flow system in presence of the catalysts investigated, heptane undergoes far-reaching transformations. The greatest extent of conversion of the heptane into isomeric paraffins and aromatic hydrocarbons is observed in presence of Pt and Pd. Under the given conditions, rhodium and ruthenium catalysts, while promoting the formation of small amounts of isomeric paraffins, cause considerable degradation, mainly to methane.

EXPERIMENTAL

Preparation of Catalysts. All catalysts were prepared by the same method under identical conditions. The silica gel, after being treated with dilute hydrochloric acid and washed with water, was heated at 500-550° for two hours. The catalysts were reduced at atmospheric pressure in a current of electrolytic hydrogen at 320-340° for eight hours.

Apparatus and Experimental Conditions

The experiments with n-heptane [b.p. (corrected) 98.5°; n_D^{20} 1.3874; d_4^{20} 0.6840] were carried out in a specially

* The spectroscopic part of this work was carried out in the Molecular Spectroscopy Laboratory of the Chemistry Department of the Moscow State University under the supervision of V. M. Tatevsky. The authors are very grateful to V. M. Tatevsky for discussions of the results of the spectroscopic determinations and for his help in the investigation.

constructed apparatus, which is shown diagrammatically in Fig. 1. The reactor 1 is a seamless steel tube of internal diameter 22 mm contained in an aluminum-bronze block heated by an electric resistance furnace. The temperature was measured with a thermocouple placed in a pocket in the reactor and was maintained at the required value within ± 3° by the aid of an electronic regulator. The hydrocarbon was passed to the reactor from the buret 3 with the aid of the dosing device 2. The latter consists of three cylinders containing pistons connected together by one common coupling rod. The piston in the middle cylinder is moved by oil delivered by the pump 4. When the piston moves from left to right, the hydrocarbon is drawn from the buret 3 into the void of the left cylinder of the dosing device, and at the same time hydrocarbon is forced from the right cylinder into the reactor. The ratio of the area of the piston of the middle cylinder to that of the left or right piston is 5:1, ensuring a low dosage rate (20 ml per hour). A low rate of dosage cannot be obtained by the direct use of the pump 3 owing to its comparatively high productivity (the lowest rate of dosage of pump 3 was 100 ml per hour) and to the lack of a satisfactory packing gland for working with low-boiling hydrocarbons. The required amount of hydrogen was passed into the reactor through the special flowmeter 7, which was graduated for the measurement of the flow of hydrogen at the experimental pressure. The catalysis products passed into the coil condenser 8 and then to the separator-receiver 9, in which the liquid hydrocarbons were separated from the gaseous products, which were passed through the gas meter 10, and then to the atmosphere or to a gas-holder for analysis.

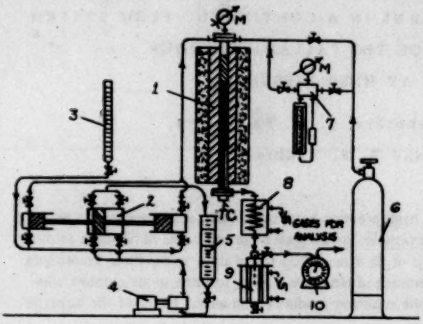


Fig. 1. Diagram of small-scale apparatus for the high-pressure reactions of hydrocarbons: 1 - reactor; 2 - dosing device; 3 - buret; 4 - pump; 5 - buret; 6 - cylinder of hydrogen; 7 - flowmeter; 8 - condenser; 9 - separator-receiver; 10 - gas meter; M - manometer; TC - thermocouple.

All experiments were carried out at 460°, the hydrogen pressure was 20 atm, and the space velocity for the passage of heptane was 1.1 liters per liter of catalyst per hour. The molar ratio of hydrogen to heptane was 5:1. The amount of each catalyst taken was 50 ml.

Investigation of Catalyzates

The liquid catalyzates were characterized by determinations of specific gravity, refractive index, and content of aromatics (by the sulfuric acid method). Hydrocarbons boiling up to 40° were first removed from the catalyzate by distillation through a 48-plate column. The aromatic hydrocarbons were then separated by chromatographic adsorption on silica gel [5], and they were fractionated through a 33-plate column. Benzene homologs were subjected to Ullmann oxidation and were identified from the melting points of the acids obtained. Paraffins were separated into fractions with the aid of a 48-plate column and these were investigated by the Raman spectrum method (the procedure and apparatus are described in the paper [6]). The gas was analyzed in an Orsat-Lunge apparatus.

Table 1 gives the properties of catalyzates obtained by the passage of heptane in presence of Pt, Pd, Rh, and Ru catalysts. It will be seen that the catalysts studied can be placed in the following order with respect to the amount of aromatic hydrocarbons formed from heptane in contact with them: Pt > Pd > Rh > Ru, whereas with respect to gas formation they must be placed in the reverse order: Ru > Rh > Pt > Pd.

Table 2 gives the properties of hydrocarbons boiling up to 40° which have been separated from the catalyzates. Comparison of the properties of the catalyzate obtained in the platinized silica gel experiment with data reported in the literature shows that the first fraction consisted mainly of isopentane, and the second mainly of n-pentane. The 29-40° fraction separated from the catalyzate obtained in the experiment with Pd–SiO_2 boiled mainly in the range 34-38°; it consisted almost entirely of n-pentane. In the heptane catalyzates obtained in the experiments with Rh and Ru catalysts, no hydrocarbons boiling below 40° were present.

Table 3 gives the fractional composition of the paraffin part of the heptane catalyzates, and Fig. 2 shows the fractionation curve for the paraffin part of the catalyzate obtained over Pt-SiO_2. Many of the fractions were investigated with the aid of their Raman spectra [6]. Thus, in the catalyzate obtained in the presence of platinized silica gel, the following hydrocarbons were identified. In Fractions I and II: 2-methylpentane 95-97% and 2,2-dimethylbutane 5-3%. In Fraction III: 2-methylpentane 45-50% and 3-methylpentane 55-50%. In Fraction IV: essentially hexane. In Fraction V: 2,4-dimethylpentane 16%, 2-methylhexane 30%, 3,3-dimethylpentane 12%, and 2,3-dimethylpentane 42%. In Fraction VI: 2-methylhexane 50-60% and 3-methylhexane 50-40%. Fractions VII and VIII were not investigated, since

they corresponded, according to their properties, to almost pure heptane.

TABLE 1

Properties of Heptane Catalyzates obtained with Pt, Pd, Rh, and Ru Catalysts

No.	Catalyst	Amount of substance passed (g)	Amount of catalyzate obtained (g)	Gas and losses (%)	Properties of catalyzate			Composition of gas (%)	
					n_D^{20}	d_4^{20}	Content of aromatics (% by volume)	H_2	C_nH_{2n+2}
1	$Pt-SiO_2$	152.6	142.0	6.9	1.4208	0.7220	20.0	93.7	6.2
2	$Pd-SiO_2$	177.2	166.5	6.0	1.3930	0.6909	7	95.3	4.7
3	$Rh-SiO_2$	113.0	93.0	18.0	1.3925	0.6904	5	35.0	65.0
4	$Ru-SiO_2$	128.4	102.7	20	1.3890	0.6855	1	32.5	67.5

TABLE 2

Properties of the Light Fractions separated from the Catalyzates before the Chromatographic Separation of Aromatic Hydrocarbons

No.	Catalyst	Boiling range (°C)	n_D^{20}	d_4^{20}	Amount (g)	Yield (% by weight on catalyzate)	Yield (% by weight on original heptane)
1	$Pt-SiO_2$	22–33•	1.3545	0.6054	8.8	6.2	5.8
		33–40••	1.3600	0.6288	10.5	7.4	6.0
2	$Pd-SiO_2$	29–40	1.3560	0.6258	2.8	2.3	1.6

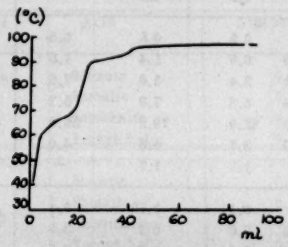


Fig. 2. Fractionation curve for the paraffin part of the heptane catalyzate obtained over a $Pt-SiO_2$ catalyst.

In the paraffin part of the heptane catalyzate obtained over $Pd-SiO_2$, the following hydrocarbons were found. In Fractions I and II: hexane 85–90% and 2- and 3-methylpentanes 5–10%. In Fraction III: 2-methylhexane 60%, 2,4-dimethylpentane 23%, 2,3-dimethylpentane 12%, and 3,3-dimethypentane 5%. In Fractions IV and V: 2-methylhexane 55–60% and 3-methylhexane 45–40%. Fractions VI and VII consisted of almost pure heptane.

In the catalyzate obtained in the experiment with $Rh-SiO_2$, Fractions II and III were found to contain 2-methylhexane 25–30%, 3-methylhexane 20–25%, and heptane 55–45%; Fractions IV and V contained mainly unchanged heptane. The possibility of the presence of some branched C_7 paraffins in Fraction IV cannot be excluded. Fraction VI was almost pure heptane.

The following hydrocarbons were identified in the catalyzate obtained from heptane in presence of $Ru-SiO_2$. In Fractions II and III: 2-methylhexane 25–30%, 3-methylhexane 20–25%, and heptane 55–45%. It is particularly noteworthy that Fraction V contained not only heptane, the content of which was 95%, but also 5% of methylcyclohexane, produced by the cyclization of heptane.

The fractional composition and properties of aromatic hydrocarbons isolated by adsorption on silica gel are given in Table 4.

The data in Table 4 show that the main aromatic product of the transformation of heptane is toluene. However, in the catalyzates obtained in experiments with Pt and Pd catalysts, small amounts of more complex benzene homologs were obtained (a 124–141° fraction, amounting to 1 g, and a 115–138° fraction, also 1 g). These hydrocarbons were submitted to Ullmann oxidation [7], and the resulting acids were separated by the method described by Moldavsky and coworkers [8]. The experimental results are given in Table 5.

• Bulk of it came over at 26–28° (754 mm).

•• Bulk of it came over at 33–35.6° (754 mm).

TABLE 3

Fractional Composition and Properties of the Paraffin Part of the Heptane Catalyzates

Catalyst	Amount of catalyzate taken for fractionation (g)	Fraction No.	Properties of fractions			Weight of fraction. (g)	Yield (%)		
			Boiling limits (°C)	n_D^{20}	d_4^{20}		on amount of catalyzate taken for fractionation	on weight of catalyzate obtained	on heptane taken for reaction
0.5% $Pt-SiO_2$	64	I	40–45	1.3610	0.6290	0.6	0.9	0.4	0.4
		II	45–60	1.3735	0.6561	2.6	4.1	1.9	1.7
		III	60–65	1.3760	0.6620	2.6	4.1	1.9	1.7
		IV	65–75	1.3805	0.6712	6.3	9.8	4.4	4.1
		V	75–90	1.3905	0.6816	4.4	6.9	3.1	2.9
		VI	90–95	1.3890	0.6851	10.8	16.9	7.6	7.1
		VII	95–98	1.3882	0.6842	30.0	46.9	21.1	19.7
		VIII	98–99	1.3885	0.6850	3.3	5.2	2.3	2.2
	Losses		–	–	–	3.3	5.2	–	–
0.5% $Pd-SiO_2$	100	I	47–60	1.3625	0.6305	1.4	1.4	0.8	0.8
		II	60–75	1.3799	0.6672	2.8	2.8	1.7	1.6
		III	75–90	1.3885	0.6856	2.3	2.3	1.4	1.3
		IV	90–95	1.3910	0.6886	11.1	11.1	6.6	6.2
		V	95–96	1.3910	0.6868	2.5	2.5	1.5	1.4
		VI	96–97	1.3885	0.6845	70.3	70.3	42.2	39.7
		VII	97–98	1.3890	0.6852	4.8	4.8	2.9	2.7
	Losses		–	–	–	4.8	4.8	–	–
0.5% $Rh-SiO_2$	66.8	I	65–80	1.3840	–	0.5	0.8	0.5	0.4
		II	80–90	1.3875	0.6840	0.9	1.4	1.0	0.8
		III	90–95	1.3887	0.6851	2.4	3.6	2.6	2.1
		IV	95–96	1.3890	0.6849	5.3	7.9	5.7	4.7
		V	96–96.5	1.3883	0.6845	52.9	79.2	56.9	46.9
	Losses	VI	96.5–101	1.3905	0.6880	3.7	5.5	4.0	3.3
			–	–	–	1.1	1.7	–	–
1% $Ru-SiO_2$	69	I	84.5–90	–	–	0.1	0.15	0.1	0.08
		II	90–95	1.3890	0.6853	3.6	5.3	3.6	2.9
		III	95–96	1.3885	0.6851	2.6	3.8	2.5	2.0
		IV	96–97	1.3885	0.6842	58.1	84.2	56.5	45.2
		V	97–100	1.3915	0.6879	3.7	5.4	3.6	2.9
			100–102.5	1.3925	0.6898				
	Losses		–	–	–	0.9	1.3	–	–

DISCUSSION OF RESULTS

The investigation of the products of the reactions of heptane at 460° in presence of Pt, Pd, Rh, or Ru deposited on silica gel and of hydrogen at 20 atm in a continuous-flow system shows that some of the original heptane undergoes dehydrocyclization with formation of toluene:

$$CH_3-(CH_2)_5-CH_3 \longrightarrow C_6H_5-CH_3 + 4H_2$$

The fact that aromatic hydrocarbons are formed over Pd and Rh catalysts is deserving of attention.

The researchers Kazansky and Areshidze did not observe the formation of aromatic hydrocarbons when

octane was passed over palladized charcoal at atmospheric pressure and at a temperature of 300-310°. It follows that changes in the chemical nature of the carrier and in the experimental conditions can result in a radical change in the properties of the catalyst and in the way in which hydrocarbons behave in contact with it. The behavior of normal alkanes over a Rh catalyst has not been studied. As will be seen from the results of our experiments, under the conditions that we have used this catalyst behaves similarly to a palladium catalyst.

TABLE 4

Properties of Aromatic Hydrocarbons isolated from the Heptane Catalyzate

Catalyst	Amount of substance taken for fractionation (g)	Fraction No.	Boiling limits (°C)	n_D^{20}	d_4^{20}	Amount of fraction (g)	Yield (% by weight)		
							on mixture taken for fractionation	on catalyzate	on original hydrocarbon
$Pt-SiO_2$	44.3	I	79.5–80	1.5005	0.8788	2.6	5.9	1.8	1.7
		II	109.5–110.6	1.4965	0.8661	36.4	82.2	25.6	23.9
		III	124–141	1.5000	–	1.0	2.2	0.71	0.7
$Pd-SiO_2$	7.2	I	108–112	1.4930	0.8620	5.2	72.3	3.1	2.9
		II	115–138	1.4960	–	1.0	14.0	0.6	0.6
$Rh-SiO_2$	4.8	I	105–109.1	1.4930	–	0.5	10.5	0.5	0.45
		II	109.1–110	1.4965	0.8664	4.0	84.0	4.3	3.5

TABLE 5

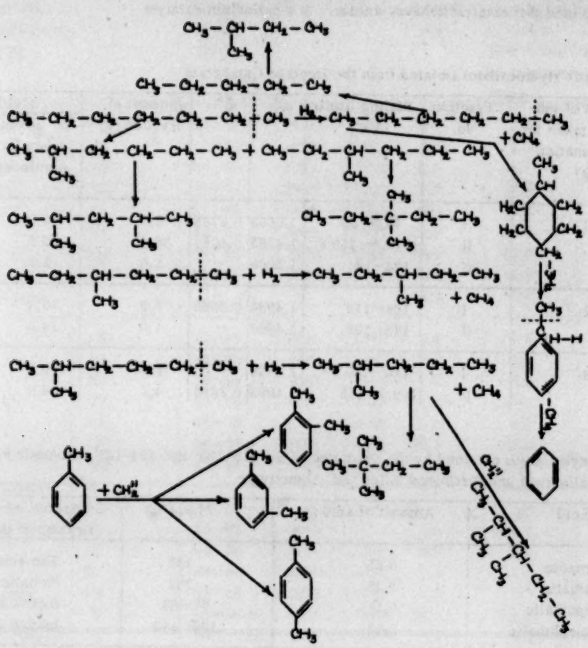
Properties of Carboxylic Acids obtained by the Oxidation of the 115-138° and 124-141° Aromatic Fractions obtained in Experiments with Palladized and Platinized Silica Gel respectively

Catalyst	Acid	Amount of acid (g)	M.p. (°C)	Compound used for the identification of the acid
$Pd-SiO_2$	Benzoic	0.25	121	The acid
	Phthalic	0.09	131	Phthalic anhydride
	Isophthalic	0.11	62–63	Methyl ester
	Terephthalic	0.05	139–140	Methyl ester
$Pt-SiO_2$	Benzoic	0.18	121	The acid
	Phthalic	0.12	131	Phthalic anhydride
	Isophthalic	0.098	63–64	Methyl ester
	Terephthalic	0.06	138–139	Methyl ester

The fact, which we are the first to observe, that methylcyclohexane (about 5%) is formed directly from heptane in presence of $Ru-SiO_2$, is of great interest. It shows that methylcyclohexane is formed intermediately in the catalytic dehydrocyclization of heptane. We shall endeavor to follow up this interesting observation in greater detail in further experimental investigations. Kazansky, Liberman, and Batuev [10] have already concluded, from a study of the products of the catalytic treatment of 3,3-dimethylhexane over platinized charcoal, that the aromatization of paraffins over platinum proceeds via the intermediate formation of six-membered cycles; these authors showed that 1,1-dimethylcyclohexane was present in the reaction product.

We consider that xylenes are formed by the methylation of toluene by methylene radicals that arise under the conditions of the experiment, and that benzene results from the partial demethylation of toluene. Under our conditions, methylene radicals may arise, on the one hand, by the breakdown of heptane, and on the other, by the breakdown of the cyclohexane hydrocarbons that are formed under the given conditions, as was shown already in 1934 by Zelinsky and Shuikin [11].

The types of catalysis product obtained, and their great variety, indicate that heptane undergoes very far-reaching transformations in presence of the investigated metal catalysts applied on a silica gel carrier.



SUMMARY

1. An investigation has been made of the reactions of heptane at 460° in a continuous-flow system in presence of Ru, Rh, Pd, and Pt deposited on silica gel and of hydrogen at 20 atm. Ruthenium, rhodium, and palladium have been applied for the first time in the study of the transformations of heptane.

2. It has been shown that, under the given conditions, heptane undergoes far-reaching transformations in various directions; apart from toluene, benzene and xylenes were found among the aromatic products. In the paraffin part of the catalyzate, C_5-C_7 branched hydrocarbons were found.

3. An appreciable amount (about 5%) of methylcyclohexane was found among the products of the catalytic treatment of heptane over Ru-SiO_2. This fact indicates that the formation of a six-membered ring occurs as an intermediate stage in the dehydrocyclization of alkanes having a chain of six or more carbon atoms.

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Received February 17, 1954

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REACTIONS OF INDIVIDUAL HYDROCARBONS IN CONTACT WITH NATURAL ALUMINOSILICATES

COMMUNICATION 2. REACTIONS OF CYCLOHEXANE, METHYLCYCLOHEXANE, AND TOLUENE IN PRESENCE OF TROSHKOV CLAY

E. A. Timofeeva and N. I. Shuikin

As is well known, catalytic cracking has now assumed great importance in the petroleum industry. A study of undoubted interest in this connection is that of the behavior of individual hydrocarbons of different classes in contact with aluminosilicates.

There are data in the literature on the cracking of cycloalkanes in presence of synthetic aluminosilicate catalysts. Frost [1] considers that naphthenes undergo cracking in contact with aluminosilicates with formation of olefins, which, as a result of isomerization and decomposition, yield branched hydrocarbons. Bloch and Thomas [2] have studied the transformations of deca- and tetra-hydronaphthalenes in presence of a synthetic zirconia-alumina-silica catalyst at 400-500°, and they have shown the catalysis processes include dehydrogenation, isomerization, ring fission, and redistribution of hydrogen. Greensfelder and Voge [3] investigated the cracking of eleven naphthenes having 6-18 carbon atoms in contact with an aluminosilicate catalyst of composition SiO_2 86.2%, ZrO_2 9.4%, and Al_2O_3 4.4% at 450-550°. These authors showed that the rate at which the cycloalkanes were broken down increased rapidly with increase in molecular weight and was independent of their structures. Thus, the degree of conversion increased from 7% for C_6 hydrocarbons to 79% for C_{18} hydrocarbons.

Maslyansky and Berlin [4], who investigated the transformations of cyclohexane over a synthetic aluminosilicate at 515-560° at ordinary pressure, established that the breakdown of cyclohexane was mainly in the direction of the formation of gaseous products, among which hydrogen and methane hydrocarbons predominated. The isomerization of cyclohexane into methycylopentane occurred only to a slight extent. In experiments of the same investigators [5] with methylcyclohexane at 515° it was shown that, apart from toluene, the reaction products contained o-, m-, and p-xylenes, ethylbenzene, trimethylbenzene, and other aromatic hydrocarbons boiling above 170°. Among the products of the transformation of methylcyclohexane, dimethylcyclopentane and also paraffin and olefin hydrocarbons were found.

Hence, in the catalytic treatment of cycloalkanes in presence of synthetic aluminosilicate catalysts at atmospheric pressure, cracking, isomerization, alkylation, ring-fission, and dehydrogenation reactions occur. The degree of conversion of the cycloalkane depends on its molecular weight; the higher the molecular weight, the higher the degree of conversion of the cycloalkane. The fact that complex aromatic hydrocarbons (xylene, trimethylbenzene) are among the transformation products of cyclohexane and methylcyclohexane is of great interest.

Thomas, Hoekstra, and Prinkston [6] have investigated the cracking of ethylbenzene, cumene, butylbenzene, and commercial amylbenzene in presence of synthetic aluminosilicate catalysts at 400-500°. They found that, when the side chain contained three or more carbon atoms, it was readily split off in the catalysis process with formation of benzene. Ethylbenzene and toluene are more stable than the higher hydrocarbons mentioned above.

A study of the literature cited shows that, although the transformations of cycloalkanes and aromatic hydrocarbons in presence of synthetic aluminosilicates have received fairly detailed investigation, there are still problems that remain to be solved. These are associated with the complexity of the process, the determination of the order in which the reactions occur, and other matters relating to the mechanism of catalytic cracking.

In our work we have studied the behavior of cyclohexane and methylcyclohexane in contact with a natural aluminosilicate (activated Troshkov clay) with the object of determining the sequence of reactions occuring in the catalytic transformations of cycloalkanes. With the same object in view we have studied also the reactions of toluene under conditions similar to those of the reactions of methylcyclohexane. As a result of these investigations we have found definite regularities in the behavior of cycloalkanes in presence of a natural aluminosilicate, and have established that in these processes the alkylation reactions proceeding concurrently with the dehydrogenation of the

cycloalkanes are predominantly important. This investigation forms a continuation of our studies of the catalytic properties of Troshkov kaolin [7, 8, 9].

EXPERIMENTAL

The pure hydrocarbons used in the investigation had the following properties:

	B.p. (corrected, °C)	n_D^{20}	d_4^{20}
Cyclohexane	80.7	1.4265	0.7787
Methylcyclohexane	100.3–100.8	1.4230	0.7699
Toluene	110.7	1.4960	0.8663

Experimental Conditions and Analytical Procedure

The catalytic treatment was carried out at 450° and 500° at atmospheric pressure at a space velocity of 0.3 in a continuous-flow apparatus. The catalyst was prepared from activated Troshkov clay. The clay was activated with sulfuric acid. The chemical composition of the clay has been stated in a previous paper [7]. All of the experiments were carried out with the same portion of catalyst (volume 100 ml, weight 92.5 g, length of layer 44.0 cm, internal diameter of catalysis tube 20 mm).

After each series of experiments with a given hydrocarbon, the catalyst was regenerated by air oxidation at 500° for 4-5 hours. The amount of sulfonatable hydrocarbons was determined by absorption in 2% oleum, and iodine numbers were determined by the Margosches method [10]. The naphthene-paraffin part of the catalyzate was separated from aromatic and unsaturated hydrocarbons by an adsorption method. The compositions of some of the catalyzate fractions were investigated by the Raman spectrum method.

Contact-catalysis Reactions of Cyclohexane

The transformations of cyclohexane were studied at 450° and 500°. The hydrocarbon was passed in 50-ml (38.9 g) portions. The properties of the resulting catalyzates are given in Table 1 (the results of typical experiments are given).

TABLE 1

Properties of Cyclohexane Catalyzates

Temperature of experiment (°C)	Yield of catalyzate (%)	Yield of gas (liters at N.T.P.)	Properties of Catalyzate				
			n_D^{20}	d_4^{20}	Sulfonatables (% by volume)	Iodine number	Unsaturated hydrocarbons (% by weight)
450	97.5	0.500	1.4260	0.7767	2.7	0.3	0.1
500	95.1	1.507	1.4265	0.7748	5.2	5.8	1.9

Analysis of gas

Temperature	450°	500°
Unsaturateds	9.6%	8.7%
Hydrogen	90.1%	87.0%
Paraffins	0.3%	4.3%

The more detailed investigation of the 450° and 500° catalyzates showed that they were approximately the same in composition. The results of the investigation of the 450° catalyzate will therefore not be given here.

Investigation of the 500° Catalyzate. The combined catalyzate from six experiments, amounting to 213 g, was separated into three parts by distillation through a 28-plate column. The properties of these fractions are given in Table 2.

Part (12.6 g) of the catalyzate fraction boiling over the range 57.0-80.4° was mixed with decane (as a "cushion") and redistilled through the same column. It yielded 8.2 g of almost pure cyclohexane (n_D^{20} 1.4260; d_4^{20} 0.7780) and 4.0 g of a fraction boiling at 65.5-78.4°(corrected) and having n_D^{20} 1.4185; d_4^{20} 0.7571. Investigation of this fraction by the Raman spectrum method showed that, apart from cyclohexane, it contained benzene, methylcyclopentane, and un-

saturated hydrocarbons (probably mainly cis-2-hexene).

TABLE 2

Properties of Fractions of Cyclohexane Catalyzates

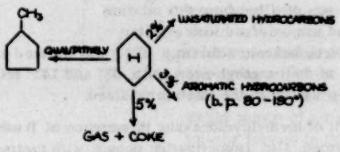
Fraction No.	Boiling limits (°C, corrected)	Amount (g)	Properties of fractions			
			n_D^{20}	d_4^{20}	Sulfonatables (%)	Iodine number
I	57.0–80.4	15.3	1.4220	0.7655	11.0	30.6
II	80.4–80.8	164.2	1.4263	0.7780	0.0	0.0
III	80.8–210.0	30.2	1.4410	0.7960	22.5	2.8
Residue		0.3	1.5240	–	–	–

The third fraction of the catalyzate (see Table 2) was freed from aromatic hydrocarbons by passage through silica gel. The resulting dearomatized fraction (29.0 g) was distilled over sodium and came over in the range 79.8-81.0° (corrected); it had n_D^{20} 1.4270 and d_4^{20} 0.7782. It corresponded in properties to cyclohexane.

The mixture of aromatic with some unsaturated hydrocarbons boiled over the range 110-190° and had n_D^{20} - 1.5170. In view of the very small amount of this fraction (0.8 g), it was not investigated in detail.

Hence, in the catalytic treatment of cyclohexane at 500° in presence of Troshkov clay, some aromatic hydrocarbons (benzene and its homologs), some unsaturated hydrocarbons, and a very small amount of methylcyclopentane were formed. No benzene was found in the 450° catalysis experiments.

The transformations of cyclohexane at 500° in contact with activated Troshkov clay may be represented diagrammatically as follows:



The overall degree of conversion of cyclohexane was 11-12%.

Contact-catalysis Reactions of Methylcyclohexane

Methylcyclohexane was passed over the same catalyst in 100-ml (77.0-g) portions. The properties of the resulting catalyzates are given in Table 3.

TABLE 3

Properties of Methylcyclohexane Catalyzates

Expt. No.	Temperature of experiment (°C)	Yield of catalyzate (%)	Yield of gas (liters at N.T.P.)	Properties of catalyzate			
				n_D^{20}	d_4^{20}	Sulfonatables (% by volume)	Iodine number
1	450	94.8	1.462	1.4195	0.7661	8.5	5.1
2	450	96.3	1.426	1.4200			
3	500	89.3	3.373	1.4228	0.7695	15.0	11.1
4	500	86.8	3.290	1.4232			

Analysis of gas

Temperature	450°(Expt. No. 1)	500°(Expt. No. 3)
Unsaturateds	15.6%	18.2%
Hydrogen	42.6%	35.7%
Paraffins	41.8%	46.1%

The results of the investigations of the 450° methylcyclohexane catalyzate will not be given, as it does not differ essentially in composition from the 500° catalyzate.

Investigation of the 500° Catalyzate. A portion (57.7 g) of the combined catalyzate from experiments carried out at 500° was separated by adsorption on silica gel into naphthene-paraffin (iodine number 25.0) parts. The curve for the fractionation of the naphthene-paraffin part of the catalyzate at 760 mm is given in Fig. 1. The properties of the fractions obtained are given in Table.4.

Owing to the very small amount available, the first fraction was not investigated. Raman spectrum analysis of the second fraction showed that it contained unchanged methylcyclohexane, heptane, 2-methylhexane, and 3-methylhexane. In the third fraction, 1,2-dimethylcyclopentane was found, and its presence is confirmed by the properties of this fraction (see the fractionation curve in Fig. 1). The fourth and fifth fractions consisted almost entirely of unchanged methylcyclohexane.

TABLE 4

Properties of Fractions of the Combined 500° Methylcyclohexane Catalyzate

Fraction No.	Boiling limits (° C)	Amount (g)	n_D^{20}	d_4^{20}	Aniline point (° C)
I	72 - 86.4	0.5	1.4080	–	–
II	86.4 - 98.0	2.9	1.4140	0.7533	50.8
III	98.0 - 100.2	8.5	1.4220	0.7700	42.7
IV	100.2 - 100.9	32.3	1.4228	0.7698	–
V	100.9 - 102.6	2.5	1.4228	0.7699	38.8
Residue		0.2	1.4310	–	–

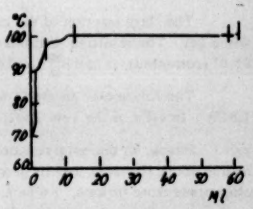
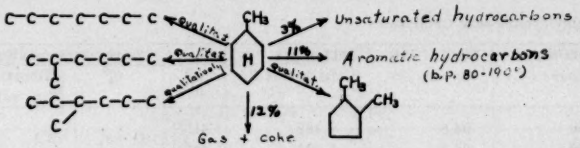


Fig. 1. Fractionation curve for the naphthene-paraffin part of the methylcyclohexane catalyzate.

The mixture (6.6 g) of aromatic and unsaturated hydrocarbons separated by adsorption boiled over the range 98-202° and had n_D^{20} and d_4^{20} 0.8357. A narrower fraction (1.8 g) was distilled from this mixture over the range 105-150° (n_D^{20} 1.4900) and was oxidized with alkaline permanganate. From the oxidation products, benzoic acid (m.p. 121°) was isolated as such, and isophthalic and terephthalic acids were isolated in the form of their methyl esters (m.p. 63° and 141° respectively). These results confirm the presence of toluene, m-xylene, and p-xylene in the fraction oxidized.

Hence, in the catalytic treatment of methylcyclohexane in presence of Troshkov clay, toluene, xylenes, and more complex benzene homologs are formed; also, isomerization occurs, with contraction of the ring from six-membered to five-membered. It is probable that, apart from these changes, cleavage of the 1,2-dimethylcyclpentane ring occurs with formation of heptane and its branched isomers. In the catalytic reaction a small amount (3 %) of unsaturated hydrocarbons is also formed.

The transformations of methylcyclohexane at 500° in presence of activated Troshkov clay may be represented diagrammatically as follows:



Degree of conversion 30 - 32%.

A comparison of the behavior of cyclohexane with that of methylcyclohexane under the conditions of catalytic treatment in presence of Troshkov clay shows that cyclohexane is much less reactive than methylcyclohexane. Thus, at 500°, the degree of conversion of the former is no more than 11-12%, while the degree of conversion of the latter under the same conditions attains 30 - 32%. Under these conditions cyclohexane yields 3% or aromatic hydrocarbons and methylcyclohexane yields 11%. No paraffins were found in the cyclohexane catalyzates, whereas in the transformation products of methylcyclohexane, heptane, 2-methylhexane, and 3-methylhexane were found.

Heptane and 3-methylhexane were formed probably as a result of the opening of the ring of 1,2-dimethylcyclopentane, which we found to be present and which was itself the product of the isomerization of methylcyclohexane with contraction of the ring. 2-Methylhexane could have been formed by the isomerization of heptane.

Contact-catalysis Reactions of Toluene

Toluene (100 ml) was passed over the same catalyst at 500° in 50-ml (43.3 g) portions. The properties of the resulting catalyzates are given in Table 5.

TABLE 5

Properties of Toluene Catalyzates

Expt. No.	Yield (% by weight)	Yield of gas (liters at N.T.P.)	n_D^{20}	d_4^{20}
1	96.8	0.308	1.4960	0.8660
2	97.0	0.495	1.4960	

TABLE 6

Properties of Fractions of Toluene Catalyzates

Fraction No.	Boiling limits (°C)	Amount (% by weight)	n_D^{20}	d_4^{20}
I	78.8–83.5	1.1	1.4998	–
II	83.5–111.8	96.5	1.4970	0.8670
III	111.8–157.8	2.0	1.5190	–
Residue		0.4	1.5300	–

The catalyzates contained traces of unsaturated hydrocarbons. The combined catalyzate (82.3 g) was fractionated through a 20-plate column into three fractions. The fractionation curve is shown in Fig. 2. The properties of the fractions are given in Table 6.

Hence, in the catalytic treatment of toluene in presence of activated Troshkov clay, about 1% of benzene and more than 2% of aromatic hydrocarbons boiling in the range 111.8-157.8° were obtained; 96.5% of the toluene remained unchanged.

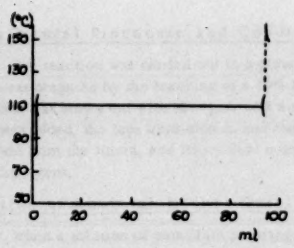


Fig. 2. Fractionation curve for the toluene catalyzate

A comparison of these results with those obtained for the transformations of methylcyclohexane results in some clarification of the sequence of reactions occurring in the catalytic treatment of methylcyclohexane. We have found that, as would be expected, toluene is stable under the given catalysis conditions; almost 97% of it remained unchanged. If the dehydrogenation of the methylcyclohexane were the primary reaction, then the bulk of the aromatic hydrocarbons formed would consist of toluene. Actually, however, the amount of toluene formed in the treatment of methylcyclohexane is much less than the amount of more complex benzene homologs. It must be supposed that under the given conditions, not only cracking and isomerization of the six-membered cycle occur, but also its alkylation by breakdown products; it is the subsequent dehydrogenation of the resulting higher cyclohexane homologs that is responsible for the formation of the corresponding aromatic hydrocarbons. However, the possibility is not excluded that in the investigated catalytic reactions of cyclohexane and methylcyclohexane, benzene and toluene formed by the dehydrogenation of these cycloalkanes may be alkylated by the same cracking products.

SUMMARY

1. A study has been made of the transformations undergone by cyclohexane, methylcyclohexane, and toluene at 450° and at 500° in contact with activated Troshkov clay.

2. It has been shown that the degree of conversion of cycloalkanes increases with rise in molecular weight; at 500°, it is 11-12% for cyclohexane and 30-32% for methylcyclohexane.

3. In the products obtained by the catalytic treatment of cyclohexane, not only benzene has been found, but also its homologs, together with methylcyclopentane and unsaturated hydrocarbons.

4. Under the same conditions, methylcyclohexane yields toluene, m- and p-xylenes, and other benzene homologs. Other products are dimethylcyclopentane, paraffins - probably formed by fission of the dimethylcyclopentane ring - and unsaturated hydrocarbons.

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Received January 22, 1954

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REACTION OF THE COMPONENTS OF SKELETAL NICKEL WITH INORGANIC OXIDANTS

L. Kh. Freidlin and K. G. Rudneva

An important characteristic of a skeletal nickel catalyst (Raney nickel) is its high chemical activity. Bougault and coworkers [1] have shown that, unlike the nickel catalyst prepared by reduction of nickelous oxide, a skeletal nickel catalyst forms a solid amalgam with mercury. Aubry [2] found that, like nickel saturated cathodically with hydrogen [3], skeletal nickel displaces copper from copper sulfate and copper acetate solutions, and it reacts readily also with sulfite, thiosulfate, and selenite solutions, and it reduces iodates, chlorates, bromates, permanganates, ferricyanides, and other inorganic oxidizing agents. Nickel prepared by reduction of nickelous oxide does not react with oxidizing agents under similar conditions. In all of these cases the reducing action of a skeletal nickel catalyst is attributed solely to the sorbed hydrogen.

The results that we have now obtained show that the reducing effect does not arise exclusively from one source: not only the hydrogen, but also the metal is involved in the oxidation-reduction process. According to the character of this process, either the hydrogen sorbed in the nickel is the main reactant, or both the hydrogen and the metal react simultaneously with the oxidizing agent.

EXPERIMENTAL

Experimental Procedure and Conditions

The reaction was carried out in a glass hydrogenation flask fitted with an outlet tube and a filter. The skeletal nickel was prepared by the leaching of a 50% Ni-Al alloy with 20% caustic soda at 100°, and it was kept under water. The flask was blown out with nitrogen, and a spoonful of the nickel paste was washed into it with water. The oxidizing agent was added, the taps were closed, and the flask was shaken mechanically at room temperature. The metal was separated from the liquid, and its residual content of hydrogen was determined. The filtrate was analyzed for residual oxidizing agent.

Reaction of Skeletal Nickel Catalyst with Potassium Permanganate

When a solution of potassium permanganate was added to a suspension of nickel in water, decolorization was rapid. The reaction was so rapid that it was not possible to make the kinetic measurements necessary to determine which of the components reacted first, the hydrogen or the nickel. It is probable that both reacted simultaneously. We have, in fact, shown in a special experiment that nickel freed from hydrogen with the aid of p-benzoquinone [4] is also able to reduce potassium permanganate rapidly at room temperature.

Reaction of Skeletal Nickel Catalyst with Sodium Iodate

A spoonful of nickel (1 g) was suspended in 10 ml of water, and the oxidizing agent was added, as a 0,6 N solution, in an amount (0.6083 g) that was in excess of the equivalent of the hydrogen contained in the catalyst. The mixture was shaken, and the shaker was stopped at short intervals of time for the taking of samples of the solution, in which residual iodate was determined iodometrically.

As will be seen from Table 1 and Fig. 1, the kinetics of the reaction of skeletal nickel catalyst with sodium iodate have the same character in their early stages as the kinetics of the reaction with p-benzoquinone [4]. During the first few minutes the reaction proceeds at an enormous rate, after which the rate falls sharply and then continues to fall. The reaction does not stop, however, even after 76 minutes from the beginning of the experiment. Thus, after the mixture had stood for two days, some more (about 0.06 g) of the oxidizing agent had been consumed. The total amount of sodium iodate consumed in this experiment was 0.5483 g, corresponding to 186.2 ml of hydrogen. The catalyst was then washed free from oxidant (tested with acidified potassium iodide solution), and was treated for one hour at 60° with 0.8014 g of p-benzoquinone in dioxane in order to determine the hydrogen remaining in the nickel after treatment with sodium iodate [4]. The determination of the hydroquinone formed showed that 39.3 ml of hydrogen remained in the nickel after the iodate treatment (Expt. No. 1, Table 2). These results give the total amount of hydrogen per 1 g of catalyst as 225.5 ml, which is about 50 ml more than the amount of hydrogen, as determined with the aid of p-benzoquinone only. It follows that after long contact sodium iodate reacts not only with hydrogen contained in the nickel, but also with the metal itself.

TABLE 1

Kinetics of the Reaction of Sodium Iodate with Skeletal Nickel Catalyst (1 g) at 20°

Test No.	Time from beginning of experiment (minutes)	Residual sodium iodate found in solution (g)	Amount of sodium iodate that reacted between the tests (g)	Amount of hydrogen (or its equivalent) removed from catalyst (ml)
1	3	0.2226	0.3857	131.0
2	8	0.1882	0.0344	11.6
3	12	0.1772	0.0110	3.8
4	16	0.1621	0.0151	5.1
5	21	0.1517	0.0104	3.5
6	27	0.1435	0.0082	2.8
7	33	0.1358	0.0077	2.6
8	44	0.1343	0.0015	0.5
9	76	0.1188	0.0155	5.3
10	After standing for two days	0.0600	0.0588	20.0
	Total amount of hydrogen removed. . .			186.2 ml

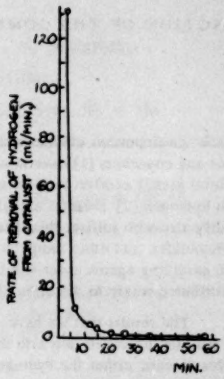

Fig. 1. Kinetics of the reaction of 1 g of skeletal nickel catalyst with sodium iodate at 20°.

TABLE 2

Hydrogen Removal from 1 g of Skeletal Nickel Catalyst with the aid of Sodium Iodate

Expt. No.	Experimental conditions		Amount consumed		Hydrogen removed (ml)			Amount of nickel oxidized (%)
			sodium iodate (g)	p-benzoquinone (g)	with the aid of		altogether	
	Temperature (°C)	Time of contact (minutes)			sodium iodate	p-benzoquinone		
1	20	76	0.4895	–	166.2	–	166.2	–
		two days	0.5483	0.1888	186.2	39.3	225.5	12.2
2	20	30	0.4125	0.2798	139.9	62.2	202.1	7.0
3	20	30	0.3067	0.3740	103.2	77.7	180.9	1.3
4	60	86	0.5482	0.1458	187.0	30.2	217.2	10.7

TABLE 3

Kinetics of the Reaction of Skeletal Nickel Catalyst (1 g) with an Alkaline Solution of Iodine at 20° (initial amount of iodine 2.8153 g)

Test No.	Time from beginning of experiment (minutes)	Duration of shaking between tests (minutes)	Amount of residual iodine found (g)	Amount of iodine that reacted between the tests (g)	Amount of hydrogen removed from the catalyst (ml)
1	3	3	1.3617	1.4534	128.0
2	7	3	1.2956	0.0661	5.8
3	11	3	1.2057	0.0899	7.9
4	16	3	1.1620	0.0437	3.8
5	20	3	1.1407	0.0213	1.9
6	26	5	1.1208	0.0199	1.8
7	32	5	1.0974	0.0234	2.0
8	43	10	1.0566	0.0408	3.6
9	54	10	1.0368	0.0198	1.7
10	77	20	1.0368	0	0
			Total amount of hydrogen removed. . . .		156.5 ml

Two further experiments were then carried out, and in these a spoonful of skeletal nickel catalyst was first treated with an insufficient amount of sodium iodate and then exhaustively with p-benzoquinone. It was considered that, if the sodium iodate reacted at first only with sorbed hydrogen but later also with metal, the total amount of hydrogen determined by the successive treatment of the nickel with sodium iodate and p-benzoquinone would be approximately equal to the amount determined by benzoquinone only, so long as an insufficient amount of sodium iodate was used.

The results confirmed this supposition. For example (Expt. No. 2, Table 2), after treatment of the nickel with 0.4125 g of sodium iodate - which corresponds to 139.9 ml of hydrogen (80% of the hydrogen contained in the metal) - a further 62.2 ml was determined as hydroquinone. The total amount of hydrogen in 1 g of nickel (202.1 ml), so determined, was only 26 ml more than the amount of hydrogen found in the nickel with the aid of p-benzoquinone. When a still smaller amount (0.3067 g) of oxidant was used (Expt. No. 3, Table 2), corresponding to 103.2 ml of hydrogen (60% of the hydrogen contained in the nickel), the further amount determined from the amount of hydroquinone formed was 77.7 ml, i.e. 180.9 ml of hydrogen altogether in 1 g of nickel. The amount found with the aid of p-benzoquinone was precisely the same. It follows, therefore, that at the beginning of the process the sodium iodate does, in fact, react only with the hydrogen. When the greater part (60-70%) of the hydrogen has reacted, slow reaction of the oxidant with the metal begins to occur concurrently with the main reaction. As in hydrogen removal with p-benzoquinone, the character of the kinetics of the process does not change when the temperature is raised from 20° to 60°.

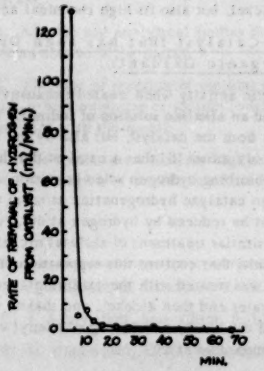

Fig. 2. Kinetics of the reaction of 1 g of skeletal nickel catalyst with an alkaline solution of iodine at 20°.

The behavior of this oxidant was greatly different from that of potassium permanganate. In the sodium iodate process it was possible to distinguish kinetically between the initial stage, in which reaction is with hydrogen only, and the subsequent stage, in which reaction with metal also occurs. In Expts. No. 2 and 3 (Table 2), in which insufficient amounts of sodium iodate were used at 20°, the amounts of metal oxidized were about 7% and 1.3% respectively, but at 60°, with an excess of oxidant (Expt. No. 4, Table 2), the amount oxidized was 11%.

We obtained similiar results in experiments on the kinetics of the removal of hydrogen from another sample of nickel with an alkaline solution of iodine at 20°. The solution was prepared by addition of 5% caustic soda solution to 0.5 N iodine until it was just decolorized. In an experiment with a 4% excess (with respect to the hydrogen in the nickel) of oxidant, almost the same amount of hydrogen was found (136.9 ml) as in an experiment with a 60% excess (156.5 ml), (Table 3). It will be seen from Fig. 2 that the kinetics of the reaction of skeletal nickel with an alkaline solution of iodine are exactly the same in character as the kinetics of the benzoquinone reaction. The inactive nickel obtained by freeing the metal from hydrogen with the aid of p-benzoquinone, does not react with an alkaline solution of iodine.

Reaction of Skeletal Nickel Catalyst with Oxygen

Bougault, Cattelain, and Chabrier [1] treated a suspension of 20 g of skeletal nickel catalyst suspended in 100 ml of water with air at room temperature for 30 days. Test samples of the catalyst were taken at intervals and analyzed for total and sorbed hydrogen. Total hydrogen was determined by dissolution of the sample in hydrochloric acid. Simultaneously, the nickel content of the solution was determined. The difference between the total hydrogen and the volume of hydrogen displaced from the acid by nickel was taken as sorbed hydrogen. It was thus shown that 1 g of the nickel contained about 140 ml of hydrogen. It was found that the total hydrogen content of the test samples fell more rapidly with time than the volume of sorbed hydrogen, from which the authors concluded that, in the course of the treatment of the catalyst with oxygen, removal of hydrogen was accompanied by oxidation of metal. Their results were qualitative.

Our new procedure has enabled us to study the rate of the process and to determine the proportions in which the oxygen is distributed between the hydrogen and the metal. When an aqueous suspension of skeletal nickel catalyst (1 g) was shaken at room temperature with oxygen in a hydrogenation flask, 101 ml of oxygen was consumed, which exceeds the amount required for the oxidation of the hydrogen contained in the nickel by 13 ml. Fig. 3

shows the rate of absorption of oxygen by the catalyst. It will be seen that absorption is most rapid in the first few minutes, and gradually falls with time. The kinetics of the reaction with oxygen differ greatly from those of the benzoquinone and sodium iodate reactions. The oxygen reaction is considerably slower, particularly in the early stages. It is probable that oxygen also is sorbed by nickel, but does not form a continuous film that would interfere with the reaction of the residual hydrogen in the metal with benzoquinone. This is in accord with the fact that, even after a 10-12-hour treatment of skeletal nickel catalyst with air under water, no nickelous oxide lines could be detected in the X-ray diagram [5].

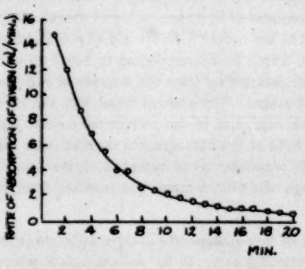

Fig. 3. Kinetics of the absorption of oxygen by 1 g of skeletal nickel catalyst at 20°.

Another sample of nickel (2 g) containing 378 ml of hydrogen was treated in the same way with an excess of oxygen, and 191 ml of oxygen was absorbed. It was then found, from the amount of hydroquinone formed in the catalyst, that there was 121 ml of residual hydrogen. Hence, only 257 (378−121) ml of hydrogen had reacted with oxygen; the remaining 63 $\left(191-\frac{257}{2}\right)$ ml of oxygen was probably consumed in the formation of a film on the nickel.

A catalyst from which hydrogen had been removed completely by means of p-benzoquinone did not react with oxygen at room temperature and pressure, from which it may be inferred that the hydrogen sorbed in the nickel determines not only the catalytic activity of skeletal nickel, but also its high chemical activity.

Reactivation of Catalyst that has been Deactivated with Inorganic Oxidants

As would be expected, skeletal nickel loses the whole of its catalytic activity when treated exhaustively with oxidizing agent (potassium permanganate, oxygen, sodium iodate, and an alkaline solution of iodine). This behavior may be explained not only by the complete removal of hydrogen from the catalyst, but also by the formation of a film having a blocking action on its surface. We have previously shown [6] that a catalyst that has been deactivated by means of p-benzoquinone will acquire the power of absorbing hydrogen when heated to only 60° (i.e. its metal-hydrogen surface will be partially regenerated) and will then catalyze hydrogenation at room temperature. Since it is probable that a surface film of nickelous oxide will not be reduced by hydrogen at 60°, it would not be expected that the same reactivation effect would be obtained by a similar treatment of skeletal nickel that has been deactivated with various oxidizing agents. We have obtained results that confirm this supposition (Table 4). The experiments were carried out as follows: 1 g of active skeletal nickel was treated with the oxidizing agent in an atmosphere of nitrogen, carefully freed from oxidant by washing with water and then alcohol, and shaken while being saturated with hydrogen at 60°. In order to determine the activity of the catalyst, 0.2495 g of phenyl vinyl ether was added in 10 ml of alcohol and the rate of absorption of hydrogen was measured at 20°.

TABLE 4

Reactivation of Catalyst that has been Deactivated with Oxidizing Agents

Oxidizing agent	Consumption of oxidizing agent per gram of catalyst, expressed as ml of hydrogen removed	Saturation of catalyst, after its treatment with the oxidizing agent, with hydrogen at 60°		Activity of the catalyst during each of the first four minutes of the hydrogenation of phenyl vinyl ether expressed as rate of absorption of hydrogen at 20° (ml/min)
		hydrogen consumed (ml)	time for saturation (minutes)	
p-Benzoquinone [4]	176.0	60	60	4.3− 1.6−1.1−1.1
O_2	159.0	12.4	20	0.6− 0.4−0.4−0.4
$NaIO_3$	192.1	0	45	0−0−0−0
$NaIO_3$	68.8	16.8	35	2.8−2.8−2.8−2.6

When skeletal nickel was exhaustively oxidized with oxygen and then shaken for 20 minutes at 60° while being treated with hydrogen, 12.4 ml of hydrogen was absorbed, and the catalyst had only a very slight activity in the hydrogenation reaction. The results of this experiment are in accord with the conclusion reached earlier, namely that the oxygen, while oxidizing the hydrogen sorbed in the nickel simultaneously forms a film on the surface of the nickel which does not prevent the nickel from again absorbing hydrogen.

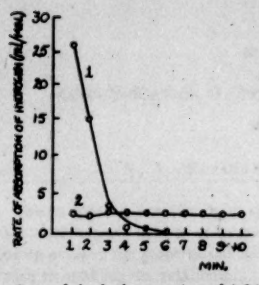

Fig. 4. Rate of the hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20°: 1 - in presence of unoxidized catalyst; 2 - in presence of catalyst oxidized with $NaIO_3$ and then treated with hydrogen.

When nickel that had been treated with an excess of sodium iodate was shaken in presence of hydrogen for 45 minutes at 60°, no hydrogen was absorbed and the nickel did not catalyze the hydrogenation of phenyl vinyl ether or of eugenol. When a catalyst (1 g) that had been treated with an insufficient amount of sodium iodate (equivalent to 68.8 ml of hydrogen) was shaken in presence of hydrogen for 35 minutes at 60°, 16.8 ml of hydrogen was absorbed, and the product had an appreciable activity for the hydrogenation of phenyl vinyl ether (Fig. 4). Confirmation is thus provided for our view that sodium iodate reacts in the first place with sorbed hydrogen, and later also with the metal, so that, during the oxidation of skeletal nickel with an excess of sodium iodate, not only removal of hydrogen occurs, but also the formation of an oxide film.

SUMMARY

1. A study has been made of the relative reactivities of the nickel and hydrogen components of a skeletal catalyst in their reaction with inorganic oxidizing agents at room temperature.

2. When the catalyst is treated with potassium permanganate, both the nickel and the hydrogen take part in the process.

3. Kinetic and analytical studies show that sodium iodate reacts primarily with the sorbed hydrogen, but reaction occurs also with the metal.

4. The rate of reaction of skeletal nickel with oxygen is much lower by a factor of 5-6 than that of its reaction with p-benzoquinone or sodium iodate. About two-thirds of the oxygen consumed reacts with hydrogen, and about one-third with the metal.

5. The results show that the high reducing power of skeletal nickel is due to the presence of sorbed hydrogen and to the high degree of dispersion of the metal itself.

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Received January 22, 1954

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 67. PROPERTIES OF POLYESTERS FORMED BY DICARBOXYLIC ACIDS WITH SOME POLYMETHYLENE GLYCOLS

V. V. Korshak, S. V. Vinogradova, and E. S. Vlasova

The relationship between the properties of polyesters and their structures has not yet received detailed consideration in the literature in spite of its great scientific importance as an essential part of the general problem of the relationship between the properties of macromolecular compounds and their structures. Only isolated attempts have been made to establish this relationship. Thus, Hill and Walker [1] attempted to show that in a homologous series of polyesters of general formula $[-O(CH_2)_nOCOCH_2(CH_2)_mCH_2CO]_x$, in which n+m had the values 14, 16, 18, and 22, the melting points varied according to a smooth curve. It follows from their results that the melting points of polyesters derived from even acids do not depend on the distribution of methylene groups between the acid and the glycol, but only on the total number of methylene groups in the repeating unit. The limited experimental data at the disposal of these authors did not permit them to make wider generalizations.

A second relevant investigation is that carried out by us on polyesters formed by 1,20-eicosanediol with the homologous series of dicarboxylic acids from oxalic to sebacic [2, 3]. It was found that the melting points of the polyesters vary according to a zig-zag line, the melting points of polyesters of dicarboxylic acids having even numbers of carbon atoms (even acids) being higher than those of dicarboxylic acids having odd numbers of carbon atoms (odd acids). An odd acid forms a polyester of lower melting point than those of the polyesters of the two neighboring even acids. When we consider the polyesters of even acids separately, it is found that there is a minimum in the curve for variation of melting point with the number of carbon atoms. On the contrary, the melting point curve for polyesters of odd acids does not show a minimum, but rises smoothly. It is not possible to make use of the data in the literature on the melting points of the individual polyesters, partly because of the gaps in these data, but mainly because of the great variation that is often found between the values given by different authors [4]. Reliable data can be obtained only by preparing all of the esters under identical conditions, and it was with this object that the present investigation was carried out.

EXPERIMENTAL

Experimental Procedure and Results

We prepared the polyesters formed by ethylene glycol, 1,6-hexanediol, and 1,10-decanediol with the following dicarboxylic acids: oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic. Oxalic and malonic acids were used in the form of their diethyl esters, and the remaining acids were applied in the free state. The experimental procedure for the polyesterification reaction has been described in detail previously [2]. An equimolecular mixture of glycol and dicarboxylic acid was heated in an atmosphere of nitrogen for ten hours at 170° and for two hours at 190°, and was then heated at a residual pressure of 2 mm Hg for two hours at 190°, for two hours at 210°, and for ten hours at 250°. The mixtures of the diethyl esters of oxalic and malonic acids with glycols were heated in a current of nitrogen for six hours at 100°, for two hours at 120°, for four hours at 140°, and for eight hours at 170°, and then under reduced pressure for five hours at 170°, for six hours at 200°, for one hour at 210°, for 90 minutes at 220°, for two hours at 230°, and for one hour at 240°. The molecular weights of the resulting polyesters were determined from the viscosities of 0.5% benzene solutions, and their melting points and solubilities in benzene and alcohol were also determined. The results are given in Table 1.

As will be seen from the data in Fig. 1, the melting points and solubilities of polyesters formed by ethylene glycol, 1,6-hexanediol, and 1,10-decanediol with dicarboxylic acids bear definite relationships not only to the total number of carbon atoms in the acid molecule, but also to the odd or even character of this number. These relationships are in general similar to those found for the polyesters of 1,20-eicosanediol, investigated previously [2,3], but certain features are more clearly expressed.

Let us examine in greater detail the dependence, first of the melting point, and then of the solubility, on the structure of the polyester, i.e. on the structures of the acid and glycol. It should be noted first of all that in the series

of polyesters formed by ethylene glycol, 1,6-hexanediol, and 1,10-decanediol, as in the series of 1,20-eicosanediol polyesters that we have already described, polyesters of even acids have higher melting points than polyesters of odd acids. This can be readily seen from Figures 1, 2, and 3, which show the dependence of the melting points of the polyesters of the respective glycols on the number of carbon atoms in the molecule of the dicarboxylic acid.

TABLE 1

Properties of Polyesters formed by Dicarboxylic Acids with some Polymethylene Glycols

Polyester	No. of atoms in repeating unit	M.p. (°C)	Solubility of polyester (g/liter of solvent)		Molecular weight
			in benzene	in alcohol	
Polyethylene oxalate	6	159–161	2.26	–	–
Polyethylene malonate	7	–22–18	3.18	–	1150
Polyethylene succinate	8	102–103	5.52	–	3760
Polyethylene glutarate	9	–19–12	180.45	–	1220
Polyethylene adipate	10	47–52	182.84	11.5	2220
Polyethylene pimelate	11	25–29	181.15	–	2620
Polyethylene suberate	12	63–65	184.08	–	1370
Polyethylene azelate	13	44–47	181.84	17.4	2400
Polyethylene sebacate	14	72–74	169.80	9.7	1180
Polyhexamethylene oxalate	10	70–72	186.12	3.06	3290
Polyhexamethylene malonate	11	–48–42	184.81	9.22	2270
Polyhexamethylene succinate	12	52–55	171.12	5.3	3300
Polyhexamethylene glutarate	13	28–34	174.08	20.0	2180
Polyhexamethylene adipate	14	55–58	189.92	8.86	3080
Polyhexamethylene pimelate	15	52–55	177.48	14.0	4650
Polyhexamethylene suberate	16	61–65	172.92	3.9	3960
Polyhexamethylene azelate	17	52–55	210.44	12.45	2520
Polyhexamethylene sebacate	18	65–68	181.16	4.90	3510
Polydecamethylene oxalate	14	76–79	165.56	–	2620
Polydecamethylene malonate	15	29–34	159.08	–	2310
Polydecamethylene succinate	16	71–73	163.36	–	4370
Polydecamethylene glutarate	17	55–58	171.16	1.5	3800
Polydecamethylene adipate	18	70–74	–	–	3340
Polydecamethylene pimelate	19	63–66	–	–	3150
Polydecamethylene suberate	20	70–75	–	–	3880
Polydecamethylene azelate	21	67–69	–	3.2	4450
Polydecamethylene sebacate	22	71–76	164.60	1.15	3270

Fig. 1 shows that the melting points of polyesters formedby ethylene glycol with dicarboxylic acids lie on a zig-zag curve. When however, the variation in melting point is considered separately for polyesters of even and odd dicarboxylic acids, two comparatively smooth curves are obtained, which are shown by the broken lines in Fig. 1. It must be stressed, however, that the courses of the two curves are greatly different, i.e. increase in the number of carbon atoms in the dicarboxylic acid affects the melting point differently in the two cases.

In the series of odd-acid polyesters a continuously rising melting point curve is obtained, whereas in the series of even-acid polyesters the melting point curve has a minimum at a point corresponding to the polyester derived from adipic acid.

The greatest change in melting point from one polyester to the next is that for the polyesters of oxalic and malonic acids; it amounts to 181°. The difference for the polyesters of malonic and succinic acids is 124°; for succinic and glutaric polyesters it is 121°; and as we proceed further the difference diminishes. In the series of polyesters derived from even acids, the greatest difference in melting point is that between the oxalic and succinic polyesters, i.e. 57°; the difference then falls, and for the suberic and sebacic polyesters it is only 10°. In the series of odd-acid polyesters, the differences in melting point are lower, the greatest difference being that for the glutaric and pimelic polyesters, namely 44°.

An examination of the melting point curve for polyesters of 1,6-hexanediol (Fig. 2) reveals a similar general picture, but the absolute values of the melting point differences are lower, and the minimum melting point in the

series of polyesters derived from even acids is that of the succinic polyester. The difference of the melting points of the oxalic and malonic polyesters of 1,6-hexanediol is 118°, i.e. less than in the ethylene glycol series.

The dependence of the melting points of polyesters formed by 1,10-decanediol with dicarboxylic acids on the number of carbon atoms in the acid is shown in Fig. 3.

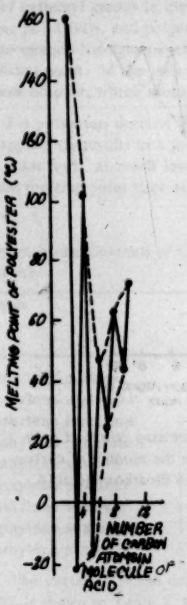

Fig. 1. Dependence of the melting points of polyesters of ethylene glycol on the number of carbon atoms in the molecule of dicarboxylic acid.

Fig. 3 shows that the greatest difference in melting points (between the oxalic and malonic polyesters) is only 47°. The variation in the melting points of the even-acid polyesters is only small, and the minimum melting point, which is that of adipic acid, is only slightly less than that of succeeding acids. In this respect the picture is similar to that which we found previously for the polyesters of 1,20-eicosanediol [2, 3].

For the characterization of intermolecular forces in polyesters, their solubilities in organic solvents are of great interest. Table 1 gives the solubilities of the polyesters in benzene and in alcohol at 20°. The solubility in benzene was determined for almost all of the polyesters, but the solubility in alcohol was determined only for a few.

It will be readily seen that the ethylene glycol polyesters of oxalic, malonic, and succinic acids have very low solubilities in benzene, and contrast greatly with the remaining polyesters, which have solubilities of higher than 160 g per liter. Polyhexamethylene azalaate is particularly soluble, being, in fact, the most soluble of all of the polyesters investigated.

Systematic determinations of alcohol-solubility were made only for the 1,6-hexanediol polyesters. The absolute solubilities are clearly much less, ranging from 3.06 to 20 g per liter, as compared with benzene-solubilities ranging to 210.44 g per liter. It is noteworthy also that, whereas the solubility in benzene does not depend to an appreciable extent on whether the polyester is derived from an even or an odd acid, the alcohol-solubilities of odd-acid polyesters are appreciably higher than those of even-acid polyesters. Thus, the solubilities of polyesters derived from even acids vary over the range 3.06-8.86 g per liter, whereas the solubilities of odd-acid polyesters vary from 9.22 to 20.0 g per liter, i.e. are appreciably higher. In Fig. 4 the dependence of the alcohol-solubilities of 1,6-hexanediol polyesters on the number of carbon atoms in the molecule of the dicarboxylic acid is illustrated graphically.

It will be readily seen that we again have a zig-zag curve, but the peaks now correspond to odd-acid polyesters, and the lower points to even-acid polyesters. This relationship is to be observed also for the other polyesters that we have synthesized, i.e. those derived from ethylene glycol and 1,10-decanediol: the azelaic polyesters were found to be more soluble than the adipic and sebacic polyesters.

Fig. 5 shows the dependence of the alcohol-solubilities of adipic, azelaic, and sebacic polyesters on the number of carbon atoms in the glycol molecule, and it will be seen that the azelaic polyesters are the most soluble, being considerably superior in this respect to the adipic and sebacic polyesters.

DISCUSSION OF RESULTS

The properties of the polyesters that we have investigated are determined by factors such as the number of methylene groups in the repeating unit, which changes as we pass from one dicarboxylic acid to the next in the homologous series, and the relative dispositions of bonds, which change as we pass from an even to an odd acid.

To understand the variations in the melting points and solubilities of the polyesters it is necessary to consider the fact that their macromolecules contain such groups as $-CH_2-$, $-CO-$, and $-O-$, which affect the melting points of compounds containing them in different ways. In previous papers [2, 3] we have given detailed consideration to the effects of these groups on the melting points of organic compounds containing them, and we shall confine ourselves here to a short summary of this material.

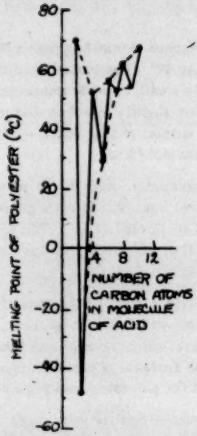

Fig. 2. Dependence of the melting points of polyesters of 1,6-hexanediol on the number of carbon atoms in the molecule of the dicarboxylic acid.

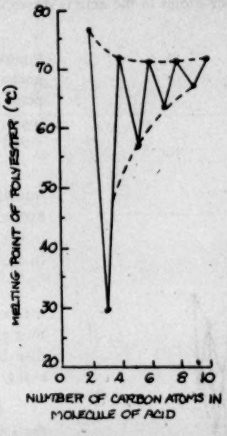

Fig. 3. Dependence of the melting points of polyesters of 1,10-decanediol on the number of carbon atoms in the molecule of the dicarboxylic acid.

Fig. 4. Dependence of the alcohol-solubilities of 1,6-hexanediol polyesters on the number of carbon atoms in the molecule of the dicarboxylic acid.

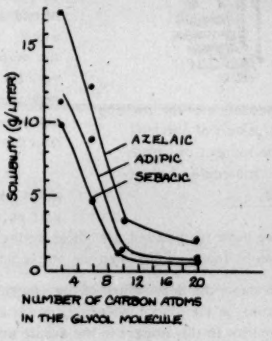

Fig. 5. Dependence of the alcohol-solubilities of polyesters of dicarboxylic acids on the number of carbon atoms in the glycol molecule.

The introduction of an ether linkage into a hydrocarbon molecule increase the flexibility of the chain because of the greater ease of rotation about the linkage −C−O−C, and therefore favors a lowering of melting point. The introduction of a carbonyl group into a hydrocarbon molecule results in a rise in melting point due to increase in the rigidity of the chain, as can be readily seen in the case of aliphatic ketones, whose melting points are higher than those of the corresponding hydrocarbons.

In polyesters, therefore, there are two opposing factors that affect their melting points: the presence of oxygen linkages, associated with a lowering of melting point in comparison with that of polyethylene; and the presence of linkages through carbonyl, associated with the raising of the melting point. To these factors must be added the evenness factor, the effect of which is particularly marked when a series of polyesters derived from even acids is compared with the corresponding series derived from odd acids. The evenness factor has not yet been completely explained, but, as we have previously pointed out [2, 3], its functioning probably depends on polar effects in the dicarboxylic acid molecules. This question will be examined in greater detail in a future paper.

If we neglect the effect of the evenness factor, then we can explain satisfactorily the courses of the melting point curves for the even-acid polyesters and for the odd-acid polyesters, which are represented by the broken lines in Figures 2, 3, and 4. For example, the anomalously high melting points and low solubilities of the first polyesters of ethylene glycol, polyethylene oxalate and polyethylene succinate can be understood when the fact that there are high proportions of carbonyl groups in these polyesters is taken into account. When the proportion of carbonyl groups is reduced, the melting point falls, and polyethylene adipate melts at 47-52°. As the proportion of carbonyl groups falls, the proportion of ester oxygen linkages also falls and the proportion of methylene groups rises, and these changes should result in a rise in melting point. In the series of even-acid polyesters derived from ethylene glycol the minimum point occurs at polyethylene adipate, which melts at 47°.

For polyesters derived from odd acids the picture is much different, owing to the operation of the evenness factor. This apparently results in a great increase in the effect of the ether linkages, so that polyesters derived from odd dicarboxylic acids melt at much lower temperatures. Increase in the content of methylene groups neutralizes this effect, so that the melting point rises as we pass from the lower odd-acid polyesters to the higher homologs.

TABLE 2

Variation in the Contents of Carbonyl Groups, Ester Oxygens, and Methylene Groups in the Series of Ethylene Glycol Polyesters.

Polyester	Number of atoms in chain of residue			Content in polyester (% by weight)		
	glycol	acid	repeating unit	carbonyl groups	ester oxygens	methylene groups
Polyethylene oxalate	3	3	6	48.27	27.58	24.14
Polyethylene malonate	3	4	7	43.08	24.61	32.31
Polyethylene succinate	3	5	8	38.88	22.22	38.90
Polyethylene glutarate	3	6	9	35.44	20.25	44.31
Polyethylene adipate	3	7	10	32.56	18.60	51.16
Polyethylene pimelate	3	8	11	30.10	17.20	52.70
Polyethylene suberate	3	9	12	28.00	16.00	56.00
Polyethylene azelate	3	10	13	26.17	14.95	58.78
Polyethylene sebacate	3	11	14	24.56	14.03	61.41

The variation in the contents of carbonyl groups, ester oxygens, and methylene groups, expressed in percentage by weight, is shown in Table 2, from which it can be seen that these contents change in a very smooth fashion, without any jumps, from one polyester to another, so that it is impossible to explain the great and sudden variations in melting point solely on the basis of the variations in the contents of carbonyl groups, ester oxygens, and methylene groups. A determining part is played here by the evenness factor, the nature of which will be considered in a later paper.

If we now return to an examination of our results, it will be readily seen that the view suggested by Hill and Walker's work [1], namely, that the melting point of a polyester depends only on the total proportion of methylene groups in the molecule and not on the way in which these methylene groups are distributed, i.e. on whether they are in the acid residue or the glycol residue, is incorrect in the general case. In illustration of this point, the melting points of polyesters having the same number of atoms in the chain of the repeating unit are compared in Table 3.

Among the ten pairs of polyesters given in Table 3, some are of the even-acid series and some are of the odd-acid series, but in no case do the melting points agree sufficiently closely to provide support for the above-mentioned hypothesis. On the contrary, the data for the ten pairs of polyesters given in Table 3 indicate that the melting points of polyesters are determined not only by the number of atoms in the chain of the repeating unit, or the number of methylene groups in the repeating unit, but also by the way in which these methylene groups are distributed between the acid and glycol residues, as can be readily seen from the examples cited.

Our results enable us to examine the dependence of the melting points of polyesters of various dicarboxylic acids on the number of carbon atoms in the glycol. This relationship is shown in Fig. 6, from which it can be seen that the melting point curves of the polyesters of oxalic, malonic, and succinic acids have minima, corresponding to the polyesters formed with 1,6-hexanediol. It is clear that for these polyesters the effect of the ester oxygen linkage attains its maximum, resulting in a maximum lowering of melting point; its effect then becomes weaker owing to the increase in the number of methylene groups, and the melting point rises. There are no minima in the curves of the polyesters of the other acids, and the melting point rises continuously as the number of methylene groups in the glycol increases. Finally, it should be noted that Fig. 6 again illustrates quite clearly that even-acid polyesters have higher melting points than odd-acid polyesters.

TABLE 3

Melting points of Polyesters having the Same Number of Atoms in the Chain of the Repeating Unit

Total number of atoms in the chain of the repeating unit	Number of atoms in the chain of the residue		Polyester	M.p.(°C)
	glycol	acid		
10	3	7	Polyethylene adipate	47 – 52
10	7	3	Polyhexamethylene oxalate	70 – 72
11	3	8	Polyethylene pimelate	25 – 29
11	7	4	Polyhexamethylene malonate	–48 – –42
12	3	9	Polyethylene suberate	63 – 65
12	7	5	Polyhexamethylene succinate	52 – 55
13	3	10	Polyethylene azelate	44 – 47
13	7	6	Polyhexamethylene glutarate	28 – 34
14	3	11	Polyethylene sebacate	72 – 74
14	7	7	Polyhexamethylene adipate	55 – 58
14	11	3	Polydecamethylene oxalate	76 – 79
15	7	8	Polyhexamethylene pimelate	52 – 55
15	11	4	Polydecamethylene malonate	29 – 34
16	7	9	Polyhexamethylene suberate	61 – 65
16	11	5	Polydecamethylene succinate	71 – 73
17	7	10	Polyhexamethylene azelate	52 – 55
17	11	6	Polydecamethylene glutarate	55 – 58
18	7	11	Polyhexamethylene sebacate	65 – 68
18	11	7	Polydecamethylene adipate	70 – 74

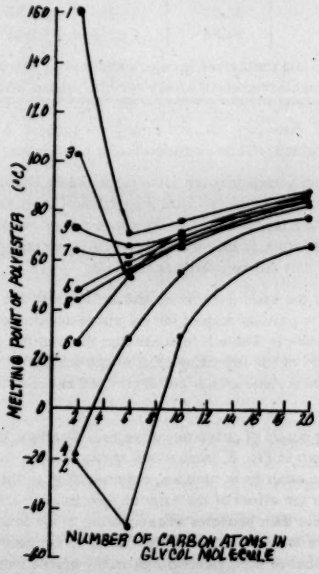

Fig. 6. Variation of the melting points of the polyesters of the following acids: 1-oxalic; 2 malonic; 3-succinic; 4-glutaric; 5-adipic; 6-pimelic; 7-suberic; 8-azelaic; 9-sebacic

SUMMARY

1. The polyesters formed by ethylene glycol, 1,6-hexanediol, and 1,10-decanediol with the following dicarboxylic acids have been prepared under identical conditions: oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids.

2. Polyesters derived from dicarboxylic acids having even numbers of carbon atoms have higher melting points than the neighboring pairs of odd-acid polyesters.

3. The solubilities of the polyesters in benzene and alcohol have been determined, and it has been found that the polyesters of the odd dicarboxylic acids have the higher solubilities in alcohol.

4. An explanation has been advanced for the way in which the properties of the polyesters depend on their structures.

5. It has been established that the melting points of polyesters depend not only on the number of methydene groups in the repeating unit, but also on their distribution within the unit.

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Received November 5, 1953

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 68. EFFECT ON THE PROPERTIES OF POLYESTERS OF THE INTRODUCTION OF ETHER OXYGENS AND SIDE CHAINS

V. V. Korshak, S. V. Vinogradova, and E. S. Vlasova

In the preceding communication we have examined the dependence of the properties of polyesters on their structures as illustrated by the behavior of the polyesters formed by ethylene glycol, 1,6-hexanediol, and 1,10-decanediol with dicarboxylic acids, namely, oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids [1]. These polyesters were prepared under identical conditions, so that we were able to compare their properties with the object of relating them to the structures of the polymers. It was found that polyesters of dicarboxylic acids having even numbers of carbon atoms in their molecules (even acids) have higher melting points than the polyesters of odd dicarboxylic acids. Similarly, the alcohol-solubilities of the former were found to be lower than those of the latter.

We considered that the variations in melting point in these series of polyesters could be explained by taking into account the effects of oxygen linkages, carbonyl groups, and methylene groups occurring in the polyester chain in various proportions and in various arrangements. With the object of establishing the part played by each of these groups in determining the properties of the polyester, we have now synthesized polyesters from glycols containing ether linkages, and we have also prepared polyesters having methyl side groups.

EXPERIMENTAL

Experimental Procedure and Results

The method of preparing the polyesters was the same as that described previously [1, 2]. The glycols used were diethylene glycol, triethylene glycol, and 1,2-propanediol, and the dicarboxylic acids were the members of the homologous series from oxalic to sebacic.

The properties of the resulting polyesters are given in the table. Their melting points and solubilities in benzene and alcohol were determined, and also their molecular weights from their viscosities in benzene solution.

DISCUSSION OF RESULTS

An examination of the tabulated properties of the polyesters permits some inferences to be made concerning the relationship between their properties and their structures. The validity of such inferences made on the basis of a comparison of these properties is increased by the fact that the polyesters were prepared under identical conditions and do not vary greatly in molecular weight.

Fig. 1 shows the curve for the variation of the melting points of polyesters prepared from diethylene glycol. It has the zig-zag form already found for the polyesters of some polymethylene glycols [1, 2], the melting points of the polyesters of even acids being higher than those of the neighboring polyesters of odd acids. The analogy cannot be carried further, however, for a comparison with the graph for the melting points of polyesters derived from polymethylene glycols immediately reveals essential differences. In the first place, the greatest differences in melting point are found for the polyesters of sebacic, azelaic, suberic, and pimelic acids, i.e. of the higher acids, whereas for the polyesters derived from polymethylene glycols, the greatest differences were found for the lower members, i.e. the polyesters of oxalic, malonic, and succinic acids. In the second place, the melting point curve of the odd-acid polyesters falls as we pass to those derived from acids containing more methylene groups, whereas the corresponding curve for the odd-acid polyesters of polymethylene glycols rises. It is clear that in the polyesters of diethylene glycol the effect of the methylene groups is completely overcome by the evenness effect and the effect of the oxygen linkages. The melting point curve for the even-acid polyesters has a very sharp minimum at the point corresponding to the polyester of adipic acid, and the rise that follows is much steeper than that on the curve for the polyesters of polymethylene glycols. It is clear that in this region the effect of the accumulation of methylene

groups is already making itself felt, and this results in a rise in melting point, as already observed for the polyesters of polymethylene glycols, the melting points of which always rise for the same reason, as we pass to the polyesters of the higher acids.

TABLE

Properties of Polyesters formed by Dicarboxylic Acids with Certain Glycols

Polyester	Number of atoms in chain of repeating unit	M.p. (°C)	Solubility of polyester (g in 1 liter of solvent) in		Viscosimetric molecular weight
			benzene	alcohol	
Poly[2,2'-oxydiethyl oxalate]	9	5 – 10	3,2	–	2930
Poly[2,2'-oxydiethyl malonate]	10	– 18 – – 11	17,4	–	2100
Poly[2,2'-oxydiethyl succinate]	11	– 11 – – 8	166,0	–	2400
Poly[2,2'-oxydiethyl glutarate]	12	– 30 – – 22	184,4	–	2440
Poly[2,2'-oxydiethyl adipate]	13	– 29 – – 24	177,8	11,3	3780
Poly[2,2'-oxydiethyl pimelate]	14	– 32 – – 26	162,2	–	3640
Poly[2,2'-oxydiethyl suberate]	15	28 – 35	160,0	–	3240
Poly[2,2'-oxydiethyl azelate]	16	– 36 – – 31	185,1	19,0	2840
Poly[2,2'-oxydiethyl sebacate]	17	44 – 46	195,8	28,2	2080
Poly[2,2'-(ethylenedioxy)diethyl oxalate]	12	– 14 – – 10	9,1	–	3660
Poly[2,2'-(ethylenedioxy)diethyl malonate]	13	– 34 – – 28	22,8	–	3160
Poly[2,2'-(ethylenedioxy)diethyl succinate]	14	– 24 – – 18	160,2	–	2240
Poly[2,2'-(ethylenedioxy)diethyl glutarate]	15	– 36 – – 28	195,5	–	2580
Poly[2,2'-(ethylenedioxy)diethyl adipate]	16	– 39 – – 30	90,8	20,6	2650
Poly[2,2'-(ethylenedioxy)diethyl pimelate]	17	– 42 – – 37	195,5	–	3180
Poly[2,2'-(ethylenedioxy)diethyl suberate]	18	– 41 – – 36	80,1	–	2820
Poly[2,2'-(ethylenedioxy)diethyl azelate]	19	– 43 – – 40	184,4	–	2160
Poly[2,2'-(ethylenedioxy)diethyl sebacate]	20	28 – 33	186,8	29,9	2450
Polypropylene succinate	8	– 2 – 0	182,9	–	1295
Polypropylene glutarate	9	– 25 – – 18	182,3	–	1790
Polypropylene adipate	10	– 25 – – 20	187,4	33,4	1130
Polypropylene pimelate	11	– 37 – – 30	189,4	–	1630
Polypropylene suberate	12	– 41 – – 34	185,0	–	1120
Polypropylene azelate	13	– 46 – – 38	180,2	28,9	1300
Polypropylene sebacate	14	– 34 – – 26	179,9	10,3	1480

The picture is somewhat different for the polyesters derived from triethylene glycol and dicarboxylic acids, as can be seen from Fig. 2, in which the melting point curve for the polyesters of triethylene glycol is given.

In this series the zig-zag form of the curve for the dependence of the melting point on the number of carbon atoms in the molecule of the acid is not completely maintained for the middle members, i.e. the polyesters of glutaric, adipic, and pimelic acids, so that the curve has a smooth section.

The melting point curve for the odd-acid polyesters falls continuously, like the corresponding curve for the polyesters of diethylene glycol. The curve for the even-acid polyesters is also very similar to the corresponding diethylene glycol curve, and its minimum corresponds to the polyester of pimelic acid. There is then a sharp rise in melting point as we pass to the polyester of sebacic acid, which may be an indication that the effect of the methylene groups is beginning to make itself felt. For the polyesters of diethylene glycol this effect begins to appear clearly at the point corresponding to suberic acid. It may therefore be stated that the addition of another ether oxygen to the molecule of the glycol neutralizes the effect of two methylene groups.

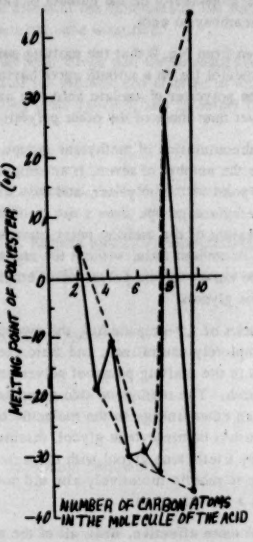

Fig. 1. Dependence of the melting points of polyesters of diethylene glycol on the number of carbon atoms in the molecule of the dicarboxylic acid.

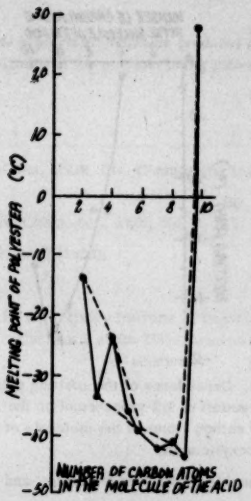

Fig. 2. Dependence of the melting points of polyesters of triethylene glycol on the number of carbon atoms in the molecule of the dicarboxylic acid.

It should be noted also that the polyesters of triethylene glycol have lower melting points than the corresponding polyesters of diethylene glycol. This evidently results from the effect of the second ether linkage, and it is analogous to the effect of the introduction of the first ether oxygen, for the melting points of the polyesters of ethylene glycol are higher than those of the polyesters of diethylene glycol, the difference being particularly great for the polyesters of even dicarboxylic acids.

It may be supposed that further increases in the number of ether linkages in the glycol will result in further smoothing of the melting point curve, so that it will finally become a smooth line. Thus, for tetraethylene glycol, and still more for pentaethylene glycol, we may expect the complete obliteration of the effect arising from an even number of carbon atoms in the acid. It may therefore be concluded quite definitely that the evenness factor and the effect of ether linkages are directly opposed to one another. The evenness factor is conducive to the formation of an ordered arrangement of macromolecules in the solid phase, whereas ether linkages facilitate the creation of a state of disorder, increasing the mobility of the macromolecules and making them less rigid, so that they no longer tend to form an ordered arrangement with respect to each other.

For the complete characterization of the properties of polyesters derived from diethylene and triethylene glycols it should be noted also that their benzene- and alcohol-solubilities, which are given in the table, are greatly different, like those of the polyesters of polymethylene glycols. The solubilities in benzene are considerably higher than those in alcohol. Also, the polyesters of oxalic and malonic acids are much less soluble than those of the other dicarboxylic acids, which have benzene-solubilities of more than 160 g per liter, with the exception of the polyesters formed by triethylene glycol with adipic and suberic acids, which are of somewhat lower solubility. The alcohol-solubilities of the polyesters rise as the number of methylene groups in the dicarboxylic acid increases, the solubilities of the polyesters formed by diethylene glycol with adipic, azelaic, and sebacic acids, for example, being 11.3, 19.0, and 28.2 g per liter respectively.

The introduction of methyl side groups into polymer molecule should have an appreciable effect on the properties of the substance. The table gives the melting points of the polyesters formed by 1,2-propanediol with dicarboxylic acids of the homologous series from succinic to sebacic. It will be seen that they are all liquids, the melting points being below 0°.

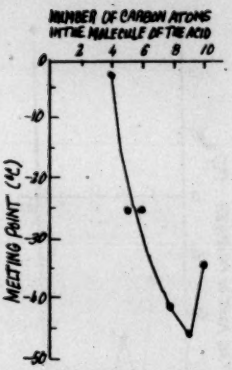

Fig. 3. Dependence of the melting points of polyesters of 1,2-propanediol on the number of carbon atoms in the molecule of the dicarboxylic acid.

Fig. 3 shows the curve for the dependence of the melting points of polyesters of 1,2-propanediol on the number of carbon atoms in the molecule of the dicarboxylic acid.

It will be seen from Fig. 3 that the melting points of the polyesters of 1,2-propanediol lie on a smooth curve having a minimum corresponding to the polyester of azelaic acid, the melting point of which (-46°) is lower than those of the other polyesters.

Hence, the accumulation of methylene groups in the dicarboxylic acid, up to the number of seven, is accompanied by a lowering of the melting point of the polyester, and only with sebacic acid, which has eight methylene groups, does a rise in melting point begin. Another peculiar feature of the melting point curve of polyesters of 1,2-propanediol is its smooth form, without the zig-zags that are so characteristic of the curves for the polyesters of ethylene glycol and other polymethylene glycols.

In the polyesters of 1,2-propanediol, the evenness factor has evidently been completely neutralized, and there are therefore no marked differences in the melting points of polyesters of even and odd dicarboxylic acids. The methylene side group has an effect similiar to that of an ether linkage in the molecule of the glycol, as seen in the polyesters of triethylene glycol, discussed above. The polyesters formed by triethylene glycol with the series of dicarboxylic acids from succinic to suberic inclusively also did not show effects attributable to the evenness factor, and their melting points fall on a smooth curve.

In this respect the introduction of methyl side groups is still more effective, since all of the polyesters of 1,2-propanediol, from the succinic to the azelaic polyester, have melting points that fall on a smooth curve. The great effectiveness of the methyl side group as an internal plasticizer is shown also by the fact that all of the polyesters that we have prepared from 1,2-propanediol are liquids, whereas only two of the polyesters of ethylene glycol were liquids at room temperature - the glutaric and malonic polyesters - the remainder being solids.

The powerful plasticizing effect of the methyl side group in polyesters of 1,2-propanediol is shown also by the fall in melting point that occurs as the number of methylene groups in the dicarboxylic acid molecule increases until we reach azelaic acid. Only when sebacic acid is reached does the curve rise, and increase in the number of methylene groups in the dicarboxylic acid begins to be accompanied by a corresponding rise in the melting point of the polyester.

We have made solubility determinations on the polyesters of 1,2-propanediol, and the results are given in the table. It will be seen from these data that the solubility of the investigated polyesters (of dicarboxylic acids from succinic to sebacic) is almost constant at about 184 g per liter. The alcohol-solubility is much lower and varies from 10.3 g per liter for polypropylene sebacate to 33.4 g per liter for polypropylene adipate, i.e. falls as the length of the methylene chain of the dicarboxylic acid increases.

In conclusion we may point out that the results of our investigations on the polyesters of diethylene glycol, triethylene glycol, and 1,2-propanediol show that the presence of an ether linkage or a methyl side group in these polyesters has a great effect on their properties. When the properties of the polyesters of these glycols are compared with those of the polyesters of polymethylene glycols (ethylene glycol, 1,6-hexanediol, 1,10-decanediol, and 1,20-eicosanediol) derived from the same dicarboxylic acids [1, 2, 3], it will be seen quite readily that the latter polyesters are crystalline substances, whereas the former are noncrystalline.

It should be noted also that, although in their general effects and ether linkage and a methyl side group are equivalent in the sense that they both reduce the crystallinity of the polymer, they differ greatly in effectiveness. If we base the comparison of effectiveness on the tendency to annul the evenness factor, then it may be said that the effect of a methyl group is equivalent to that of three or four ether linkages, i.e. one methyl side group is three or four times as effective as an ether linkage.

SUMMARY

1. Some polyesters formed by diethylene glycol, triethylene glycol, and 1,2-propanediol with dicarboxylic

acids have been prepared.

2. The effect of the structures of the starting substances on the melting points and solubilities of the resulting polyesters has been discussed.

3. It has been shown that the introduction of a methyl side group into a polyester molecule produces an effect similiar to that of the introduction of three or four ether linkages, the crystallinity of the polymer being greatly reduced, its melting point lowered, and its solubility raised.

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Received November 5, 1953

N. D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

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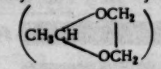
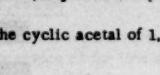
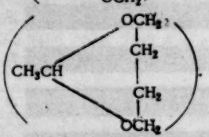
THE OXONIUM THEORY IN THE LIGHT OF AN OPTICAL STUDY OF THE HYDROGEN BOND IN SOME MONOVINYL ETHERS OF GLYCOLS AND POLYGLYCOLS

M. F. Shostakovsky, M. I. Batuev, P. V. Tyupaev, and A. D. Matveeva

One of the authors of this paper has suggested [1], in connection with the oxonium theory that he has developed on the basis of the reactions of vinyl ethers, that in these compounds the valency of oxygen is variable: according to the conditions, the oxygen behaves as a bi- or ter-valent element.

The history of investigations on oxygen-containing compounds shows that for oxygen in various compounds under various experimental conditions authors have suggested valencies not only of two and three, but also of four, and even six*. It would, of course, be of great interest to determine the nature of the observed or postulated "anomalous" valency of oxygen in these and other cases, and so determine the structures of the oxygen-containing compounds. The present investigation is a structural study of this sort applied to some vinyl ethers, which have been examined with the aid of Raman spectra. At the same time we have investigated some cyclic acetals that are isomeric with these ethers.

The following monovinyl ethers of glycols and "polyglycols", and cyclic acetals isomeric with these, were synthesized and investigated optically: 1) the monovinyl ether of ethylene glycol ($CH_2=CH-O-CH_2-CH_2-OH$); 2) the monovinyl ether of 1,3-propanediol ($CH_2=CH_2-O-CH_2-CH_2-CH_2-OH$); 3) the monovinyl ether of 1,4-butanediol ($CH_2=CH-O-CH_2-CH_2-CH_2-CH_2-OH$); 4) the monovinyl ether of diethylene glycol ($CH_2=CH-O-CH_2-CH_2-O-CH_2-CH_2-OH$); 5) the monovinyl ether of triethylene glycol ($CH_2=CH-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-OH$);
6) the cyclic acetal of ethylene glycol  ; 7) the cyclic acetal of 1,3-propanediol 
8) the cyclic acetal of 1,4-butanediol  .

1. Synthesis of Minovinyl Ethers of Glycols and Polyglycols and of Cyclic Acetals of Glycols

The monovinyl ethers of ethylene glycol, 1,3-propanediol, 1,4-butanediol, diethylene glycol, and triethylene glycol were prepared by Favorsky and Shostakovsky's method [4] by the addition of 0.8-1 mole of acetylene to 1 mole of the glycol or polyglycol containing about 5% of dissolved caustic potash as catalyst. The preparations were carried out, similarly to that of the monovinyl ether of ethylene glycol described previously [5], in a rotating autoclave under a pressure of not more than 15 atm and at a temperature of 140-150°. The yields of the ethers varied from 40% to 60% on the amount of glycol that reacted. The reaction products were fractionated from a Favorsky flask. The monovinyl ether fractions taken were too wide to correspond to pure products. They were dissolved in water with the object of separating them from the somewhat lower boiling water-insoluble divinyl ethers. The solutions were separated from the divinyl ethers (sometimes by the aid of the salting-out effect of a small amount of potassium carbonate), and were then saturated with potassium carbonate. The salted-out monovinyl ethers were separated, dried carefully with potassium carbonate, and fractionated in presence of a small piece of calcined potassium carbonate in an apparatus having ground glass joints (including the thermometer). The fractions were redried before each redistillation. Products having definite constants were finally obtained.

The cyclic acetals of ethylene glycol, 1,3-propanediol, and 1,4-butanediol were prepared by the isomerization of the corresponding pure monovinyl ethers, which generally occurs almost instantaneously in presence of mineral

* For a more detailed discussion of this see our preliminary communications [2, 3].

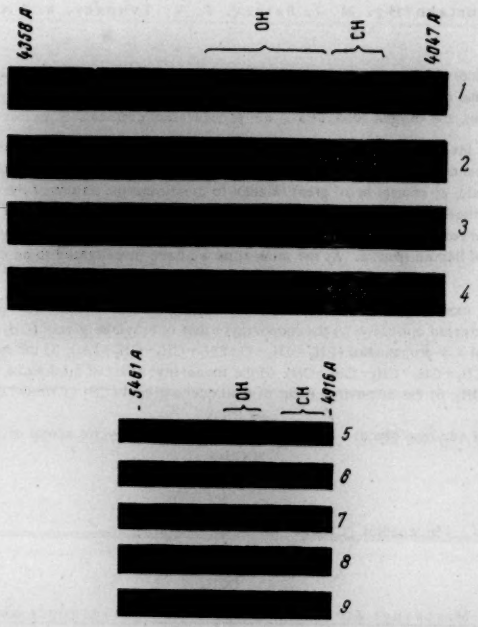


Fig. 1. Spectra of the hydroxyl groups of hydroxyl-containing compounds. Excited by the triplet 3650, 3655, 3663 A: 1) formic acid 2) methanol; 3) phenol (1, 2, and 3 are for comparison purposes); 4) monovinyl ether of ethylene glycol. Excited by the blue line 4358 A: 5) monovinyl ether of ethylene glycol; 6) monovinyl ether of 1,3-propanediol; 7) monovinyl ether of 1,4-butanediol; 8) monovinyl ether of diethylene glycol; 9) monovinyl ether of triethylene glycol.

acids, much heat being evolved. The reaction was carried out in a three-necked flask fitted with reflux condenser, mechanical stirrer, thermometer, and dropping funnel. A few drops of concentrated hydrochloric acid were placed in the flask, and the vinyl ether was then added. At first the temperature was not allowed to rise above 80°, but later the reaction mixture was brought to the boil. After cooling, it was neutralized with 1-2 ml of 10% caustic soda, dried with potassium carbonate, and distilled. The resulting acetals were treated in the cold with sodium and then distilled in absence of the sodium in an apparatus having ground glass joints (including the thermometer). The fractions were retreated with sodium before each distillation. Products having definite constants were finally obtained. The cyclic acetals of ethylene glycol and 1,3-propanediol were obtained in yields of not less than 90%, but the yield of the cyclic acetal of 1,4-butanediol was not more than 50%.

The table gives the constants of the synthesized monovinyl ethers of glycols and polyglycols and of the three cyclic acetals.

TABLE

Constants of Monovinyl Ethers of Glycols and Polyglycols and of Cyclic Acetals that are Isomeric with some of these

Substance	B.p. (°C) (p, mm Hg)	d_4^{20}	n_D^{20}
Monovinyl ether of ethylene glycol	140(745)	0.9821	1.4360
Monovinyl ether of 1,3-propanediol	164(755)	0.9611	1.4390
Monovinyl ether of 1,4-butanediol	182(755) 74.5 (7)	0.9467	1.4458
Monovinyl ether of diethylene glycol	96 (12)	1.0278	1.4480
Monovinyl ether of triethylene glycol	144 (14)*	1.0525	1.4536
Cyclic acetal of ethylene glycol	81–2(750)	0.9795	1.3972
Cyclic acetal of 1,3-propanediol	107(740)	0.9683	1.4125
Cyclic acetal of 1,4-butanediol	127–128(750)	0.9638	1.4280

2. Raman Spectra of the Synthesized Monovinyl Ethers of Glycols and Polyglycols and of Cyclic Acetals that are Isomeric with some of these

The Raman spectra of the synthesized monovinyl ethers and cyclic acetals were determined with a Soviet - spectrograph ISP-51 having a central camera. The dispersion in the region of the line 4358 A was 26 A/mm. The spectra were excited by the mercury line 4358 A. In addition, the region of the hydroxyl group of monovinyl ethers was investigated with the mercury triplet 3650, 3655, 3663 A as exciting radiation. We give the complete Raman spectra for the substances investigated below. The intensities of the lines are given in parentheses on a visual ten-grade scale **.

Monovinyl ether of ethylene glycol, $\Delta\nu$ (cm^{-1}): 246(4); 296(0); 316(2); 334(3); 356(1); 500(4b); 606(3b); 656(0); 704(3b), 810(2); 831(8); 870(0); 892(3b); 943(2); 968(x); 979(3); 1003(0); 1031(3b); 1096(3b); 1154(2); 1174(2); 1203(2); 1233(2); 1281(3); 1320(10); 1359(2d); 1893(2); 1414(2); 1459(4); 1617(7); 1638(6); 2660(0); 2722(0); 2879(6)* 2933(10)*, 2964(2)*; 3024(6); 3044(10); 3085(0); 3120(7); ~3200–3600(3, band);

Monovinyl ether of 1,3-propanediol, $\Delta\nu$ (cm^{-1}): 250(3, band); 355(2b); 409(0); 497(3b); 597(2); 654(0); 686(0); 707(2); 814(5); 830(5); 870(5); 891(5); 957(3); 968(3); 1003(2); 1044(4)*; 1075(4)*; 1104(4)*; 1208(3)*; 1234(0); 1297(4); 1324(10); 1355(0); 1384(1); 1418(2); 1443(1); 1478(5); 1618(7); 1643(6); 2880(6)*; 2941(9)*; 2960(2)*; 3022(4); 3047(7); 3119(5); ~3200–3600(3, band).

Monovinyl ether of 1,4-butanediol, $\Delta\nu$ (cm^{-1}): 214(0); 247(6b); 303(3b); 346(0); 398(1); 450(2); 500(4); 531(1); 554(1); 588(0); 608(3); 630(0); 655(0); 679(0); 708(3); 755(1); 784(0); 823(8b); 863(3); 901(0b); 940(4)*; 971(4)*; 999(2)*; 1052(5)*; 1074(5)*; 1102(6)*; 1137(2); 1299(6); 1324(10); 1352(0); 1378(2); 1416(1); 1438(6); 1456(1); 1477(6); 1615(8); 1643(7); 2744(2)*; 2821(2)*; 2868(10b)*; 2927(10b)*; 2963(6)*; 3019(6); 3046(9); 3079(0); 3121(9); ~3200–3600(3, band).

Monovinyl ether of diethylene glycol, $\Delta\nu$ (cm^{-1}): 216(1); 243(4b); 289(0); 324(0); 435(0); 496(3)*; 528(2)*; 557(3)*; 611(3b); 654(0); 720(3b); 807(5)*; 849(5)*; 892(4); 962(1); 980(4); 1008(0); 1037(4)*; 1071(4)*; 1131(5b)*; 1261(3)*; 1290(3)*; 1323(10); 1455(5); 1471(5); 1620(8); 1636(6); 2877(10)*; 2942(9b)*; 3024(3); 3044(7); 3117(5); ~3200–3600(3, band).

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* In a previous paper [3] the boiling point of the monovinyl ether of triethylene glycol is also given as 144° at 14 mm.

** The symbols appended to the intensity figures are: b - broad line, d - double line; the asterisk indicates lines having an intense background.

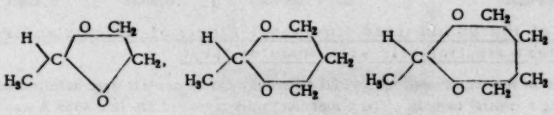
Monovinyl ether of triethylene glycol, $\Delta\nu$ (cm^{-1}): 214(1); 240(4b); 293(0b); 341(0b); 404(0b); 459(0b); 500(3)*; 541(2)*; 559(2)*; 589(2)*; 623(2)*; 660(0); 807(5)*; 830(5)*; 849(5)*; 887(3); 911(0); 931(0); 973(2b); 1013(0); 1041(3)*; 1081(2)*; 1133(4)*; (5)*; 1200(1)*; 1237(2)*; 1279(3)*; 1296(3)*; 1324(0); 1400(2b); 1454(5); 1473(5); 1617(8); 1639(6); 2855(2)*; 2874(10)*; 2945(9b)*; 3022(3); 3042(6); 3083(0); 3119(4); ~3200–3600 (3, band).

Cyclic acetal of ethylene glycol, $\Delta\nu$ (cm^{-1}): 175(0); 510(4b); 537(0); 693(3); 838(10); 922(0); 945(9); 1025(5b); 1091(0); 1120(6b); 1149(1); 1171(4); 1222(6b); 1282(0); 1315(3); 1356(3); 1390(0); 1413(0); 1452(6); 1481(6); 2885(6b); 2939(10); 2992(5b).

Cyclic acetal of 1,3-propanediol, $\Delta\nu$ (cm^{-1}): 274(0); 349(0); 432(0); 461(6); 480(2); 501(0); 523(0); 546(0); 567(7); 589(0); 610(0); 633(0); 656(0); 680(0); 714(0); 744(0); 821(10); 855(0); 878(5); 899(0); 922(0); 935(6); 971(6); 1027(0); 1058(6); 1104(6); 1148(7); 1179(2); 1219(4); 1246(2); 1286(7); 1343(2); 1375(4)*; 1433(5); 1454(6); 1468(6); 2644(0); 2668(3); 2704(0); 2733(3); 2814(0)*; 2857(10)*; 2921(2)*; 2941(10)*; 2970(3)*; 2996(6)*.

Cyclic acetal of 1,4-butanediol, $\Delta\nu$ (cm^{-1}): 207(2); 309(3); 341(4); 384(4); 428(6); 472(0); 496(0); 520(0); 542(5); 575(0); 621(1); 642(1); 779(10); 820(2); 840(2); 858(0); 922(2); 940(6); 973(6); 997(2); 1024(0); 1056(6)*; 1078(4)*; 1097(2)*; 1132(7)*; 1147(1)*; 1179(1)*; 1233(6); 1251(0); 1275(0); 1288(8); 1340(2)*; 1362(3)*; 1434(8); 1448(8); 1463(8); 2707(0); 2746(0); 2817(0)*; 2846(4)*; 2879(8)*; 2915(8)*; 2945(10)*; 2993(7)*.

There are essential differences between the spectra of the monovinyl ethers of the glycols and those of the corresponding isomeric cyclic acetals, particularly the absence in the latter of the frequencies in the neighborhood of 1600 cm^{-1} (double bond region) and in the region above 3000 cm^{-1} (ther frequencies of C – H at a double bond and of the hydroxyl group). We have made use of these essential differences in the optical analysis of some solutions of the investigated monovinyl ethers, as will be seen below. In passing, we may point out the lowering of the "pulsation" frequency of the ring as we proceed from a five- to a seven-membered ring in the cyclic acetals, a phenomenon observed also in the corresponding cycloalkanes:



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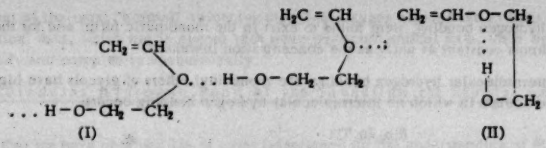
3. Optical Detection of the Hydrogen Bond in Monovinyl Ethers of Glycols and Polyglycols.

The above-cited spectra of monovinyl ethers of glycols and polyglycols, unlike those of the cyclic acetals investigated, contain frequencies in the region 3000-3120 cm^{-1} characteristic of vibrations of C – H bonds occurring at double bonds C = C, and also frequencies in a broad diffuse band in a still higher region, this being practically the same for all of the five ethers investigated, about 3200-3600 cm^{-1}. This is the region of the hydroxyl frequencies.

In Fig. 1 we show this band for the spectrum of the monovinyl ether of ethylene glycol (Spectrum No. 4), the exciting radiation being the triplet 3650, 3655, 3663 A. For the other ethers investigated the band is quite similar, as will be seen from a comparison of the corresponding regions of the spectra excited by the line 4358 A (Spectra No. 5-9). For comparison we give in Fig. 1 the spectra for the hydroxyl groups of liquid formic acid, methanol, and phenol (Spectra No. 1-3). It has been established that the presence of a broad hydroxyl band in the spectra of these substances is an indisputable criterion of the participation of the hydroxyl groups of these substances in intermolecular hydrogen bonds. An equally indisputable criterion of intermolecular hydrogen bonding is to be found in the broad diffuse band at 3200-3600 cm^{-1} that we have observed in the spectra of all five of the monovinyl ethers investigated, this band being identical in general features to the hydroxyl bands of methanol, acetic acid, and phenol (we shall not consider the differences in detail in the present paper). The considerable breadth of the band and its considerable diffuseness on the low-frequency side indicates that the hydrogen bonds of monovinyl ethers of glycols and polyglycols are indeed intermolecular bonds of the type (I), and not intramolecular bonds of the type (II) [6]; if the latter are formed, then it must be at the ends of the chain (I):



(I) (II)

The intermolecular character of the hydrogen bonds of these monovinyl ethers is confirmed also by other physicochemical properties, which we shall consider below.

As is well known, the spectrum of the hydroxyl group of a molecule under conditions (in the gas phase, or dissolved in neutral solvents of the type of carbon tetrachloride, cyclohexane, benzene, etc.) which prevent hydrogen bonding is fundamentally different from that of the hydroxyl group in the liquid phase of the substance, when a hydrogen bond is formed *.

When, however, the investigated monovinyl ethers of glycols are dissolved in carbon tetrachloride, optical analysis shows that they isomerize into the corresponding cyclic acetals; no monovinyl ether molecules are present. This fact is readily established optically because of the considerable differences, noted above, between the spectra of the investigated monovinyl ethers and those of the corresponding isomeric cyclic acetals. This isomerization occurs not because the isolated molecules of the ethers are in themselves unstable and therefore undergo rearrangement into cyclic acetals, but because of the nature of the solvent, carbon tetrachloride.

The investigated monovinyl ethers are almost insoluble in cyclohexane, and two layers are formed when they are mixed. One layer is the monovinyl ether as such, and the very small portion of the monovinyl ether that passes into the cyclohexane layer does not isomerize into the cyclic acetal, as spectrum analysis shows. It is evident that in this solution vinyl ether molecules exist in the isolated state, as monomers. However, confirmation of this cannot be obtained by observations on the change in the spectrum of the hydroxyl group owing to the extremely low intensity of the hydroxyl lines resulting from the very low concentrations of the solutions, which, in their turn, are to be attributed to the very poor solubilities of the monovinyl ethers in cyclohexane.

We therefore modified the hydroxyl spectrum via a rise in temperature, determining the spectrum of monovinyl ether of ethylene glycol at a temperature of about 85°. Owing to partial disruption of the hydrogen bonds, and also to the weakening of the hydrogen bonds that still existed, the hydroxyl band became narrower under these conditions and the intensity maximum was displaced toward the higher frequencies**. At the high-frequency limit of the band there was a readily measurable line (a triplet record was obtained from the exciting triplet 3650, 3655, 3663 A) at 3565 cm^{-1}. The comparatively low value of this frequency (for monomeric molecules of aliphatic monohydric alcohols, e.g. methanol, it attains a value of about 3670 cm^{-1} in the gas phase) and its position at the high-frequency limit of a hydroxyl band of reduced breadth indicate that in the liquid state raising of the temperature to 85° does not result in the complete freeing of the hydroxyl groups from the influence of oxygen atoms of neighboring molecules. When, in fact, a 20% (by volume) solution of the monovinyl ether of ethylene glycol in decalhydronaphthalene is heated to 85°, a line of still higher frequency is observed in the hydroxyl spectrum, namely 3625 cm^{-1} (a triplet record from the exciting triplet 3650, 3655, 3663 A). Under these conditions decahydronaphthalene molecules isolate molecules of the monovinyl ether of ethylene glycol from one another, and the hydroxyl group is freed from the influence of the oxygens of other molecules of the monovinyl ether of ethylene glycol. The fact that the frequency of the hydroxyl group of the monomeric molecule of the monovinyl ether of ethylene glycol is nevertheless lower than that of the hydroxyl group of monomeric molecules of monohydric alcohols will be referred to again below.

4. Confirmation of the Optical Detection of a Hydrogen Bond in the Investigated Ethers by means of other Physicochemical Data

The presence of the hydrogen bond indicated by optical methods is confirmed by other physicochemical data. Thus, we have carried out molecular weight determinations on all five of the ethers investigated. It was found that with rise in concentration the degree of association increased: the monomers were converted into associated complexes, first of all dimers, and later polymers (see Fig. 2). The isomeric cyclic acetals, which would not

* See the photograph in a paper by one of the authors [7] of the spectrum of a hydroxyl group that is not hydrogen-bonded (in the monomeric molecule of acetic acid in the gas phase), when it takes the form of a sharp line, and the spectrum of a hydroxyl group that is hydrogen-bonded (in liquid acetic acid), when it takes the form of a broad diffuse band displaced toward the lower frequencies.

** One of the authors of this paper has established that phenol behaves similarly [8].

be expected to exhibit hydrogen bonding, were found to exist in the monomeric form, and for them the degree of association remained almost constant at unity as the concentration increased.

As a result of intermolecular hydrogen bonding, the monovinyl ethers of glycols have higher boiling points than the isomeric cyclic acetals in which no intermolecular hydrogen bonding occurs:

	B.p. in °C (p in mm Hg)		B.p. in °C (p in mm Hg)
Monovinyl ether of ethylene glycol	140 (745)	Cyclic Acetal of ethylene glycol	81–82 (750)
Monovinyl ether of 1,3-propanediol	164 (755)	Cyclic Acetal of 1,3-propanediol	107 (740)
Monovinyl ether of 1,4-butanediol	182 (755)	Cyclic Acetal of 1,4-butanediol	127–128 (750)

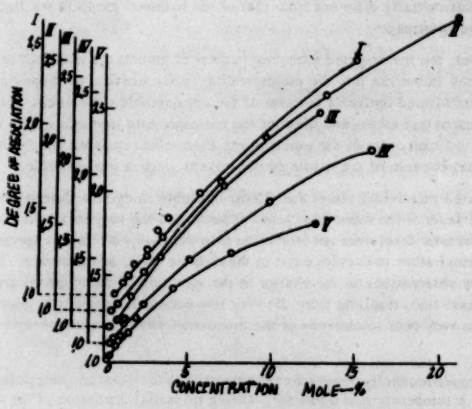


Fig. 2. Degree of association of I - monovinyl ether of ethylene glycol; II - monovinyl ether of 1,3-propanediol; III- monovinyl ether of 1,4-butanediol; IV- monovinyl ether of diethylene glycol; V- monovinyl ether of triethylene glycol; expressed as functions of the concentrations of their solutions in benzene(determined by the cryoscopic method)

The nonhydrogen-bonding cyclic acetals have also considerably lower viscosities than the corresponding ethers from which we obtained them by isomerization (viscosities in centipoise at 20°):

Monovinyl ether of ethylene glycol	2.4167
Monovinyl ether of 1,3-propanediol	4.0412
Monovinyl ether of 1,4-butanediol	5.7551
Monovinyl ether of diethylene glycol	5.2651
Monovinyl ether of triethylene glycol	9.8670
Cyclic acetal of ethylene glycol	0.6499
Cyclic acetal of 1,3-propanediol	0.8544
Cyclic acetal of 1,4-butanediol	1.0902

(The viscosities were determined in a Pinkevich capillary viscometer having a capillary of diameter 0.8 mm. The viscometer was calibrated with water, the viscosity of which was taken as 1.0050 centipoise at 20°. The viscometer was placed in a thermostat at 20°, and the rate of efflux was measured 30 minutes after the liquid had been introduced into the viscometer.)

Hence, the intermolecular hydrogen bonding that we detected in monovinyl ethers of glycols and polyglycols by the optical method has been unequivocally confirmed by other physicochemical data cited above. At the same time the nature of the "anomalous" valency of oxygen in the investigated ethers, which we referred to at the beginning of the paper, has been elucidated quite unequivocally: it consists in the ability of oxygen atoms in the ethers investigated to form hydrogen bonds with the hydroxyl groups of neighboring molecules as an effect

supplementary to that of the usual "normal" valencies that these oxygen atoms have at their disposal. By means of experimental optical data, which are in accord with other physicochemical data, these hydrogen bonds have been detected directly and completely unequivocally.

5. The Intermolecular Hydrogen Bond of the Investigated Ethers, and their Chemical Properties

The results that we have obtained are of great importance for the understanding of the behavior of various vinyl ethers, differing from one another in composition and structure.

Thus, it has been established in previous investigations by Shostakovsky and coworkers that alkyl vinyl ethers are highly reactive (readily undergoing various reactions, particularly in presence of mineral acids and metal chlorides), whereas monovinyl ethers of glycols are chemically inert. In the light of our results, this is easily understood. Thus, we regard the activation of alkyl vinyl ethers by mineral acids as the formation via a hydrogen bond of complexes that can isomerize and dissociate:

$$CH_2 = CH - O - Alk$$
$$\vdots$$
$$HCl$$

It will be clear, however, that monovinyl ethers of glycols cannot behave in this way, since their structures already contain hydrogen bonds. This is also the basis of the chemical inertness that we have established experimentally.

There can be no doubt that this inertness must be shown also by monovinyl ethers of polyglycols, though it is probable that it will not be so great, since their ether oxygens, unlike those of monovinyl ethers of glycols, cannot all take part in hydrogen bonding (in monovinyl ethers of polyglycols there are several ether oxygens per hydroxyl group).

There is a further point that is worthy of notice. We have already pointed out that in comparison with the frequency of the hydroxyl group in monohydric alcohols, the frequency of the hydroxyl is low in monovinyl ethers of glycols and polyglycols in which hydrogen bonding has been completely, or almost completely, broken down by rise in temperature to 85° in the liquid phase or by dissolution in decahydronaphthalene. This fact undoubtedly indicates that the hydrogen of the hydroxyl group of the investigated ethers in their monomeric form is more mobile than that of monohydric alcohols [7]. This view is confirmed by the following chemical data.

A study of the effect of temperature in the vinylation of monohydric alcohols (methyl, ethyl, and butyl), glycols, and polyglycols has shown that the addition of C_2H_2 to monohydric alcohols begins only at 150°, whereas glycols and polyglycols already react at 140°. In view of the fact that the formation of the divinyl ether proceeds stepwise (via the monovinyl ether) and that the products of the complete vinylation of glycols at 140° comprise only the divinyl ethers with insignificant amounts of the cyclic acetals (the formation of which occurs in the gas phase owing to the isomerization of the monovinyl ethers), it must be acknowledged that the hydrogens of the hydroxyls of glycols and polyglycols, and also of the hydroxyls of the monovinyl ethers of glycols and polyglycols, have practically identical mobilities, which are appreciably higher than the mobilities of the hydrogens of the hydroxyls of monohydric normal aliphatic alcohols.

SUMMARY

An optical investigation of some monovinyl ethers of glycols and polyglycols has indicated the presence of intermolecular hydrogen bonds in the liquid state, and this is confirmed by data derived from other physicochemical investigations. The presence of an intermolecular hydrogen bond explains the "anomalous" valency of the oxygen atom of the investigated class of ethers (its "oxonium" character), and also peculiarities of the properties of these ethers.

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Received September 10, 1953

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SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

COMMUNICATION 5. VINYL ETHERS OF DI- AND TRI-ETHANOLAMINES

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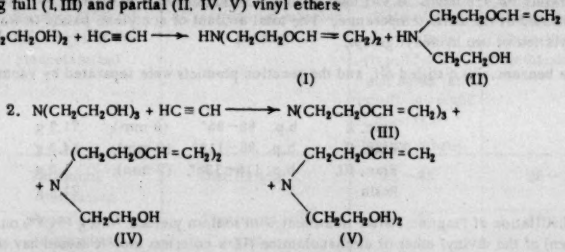
In order to determine the relationship between structure and reactivity for vinyl ethers of ethanolamines we have investigated the properties of several such substances in which the substituents present on the nitrogen were varied. In continuation of our previous investigations [1, 2, 3] we have studied the properties of vinyl ethers of di- and tri-ethanolamines. These compounds were synthesized by direct vinylation of the ethanolamines, which may yield a number of products under the conditions of the Favorsky-Shostakovsky reaction [4] owing to the presence of more than one hydroxyl group in the molecules of these substances. The vinylation of these ethanolamines did in fact yield the corresponding full (I, III) and partial (II, IV, V) vinyl ethers:



In this respect di- and tri-ethanolamines are similar to ethylene glycol and glycerol [5, 6], but the vinyl ethers of di- and tri-ethanolamines did not undergo further changes resulting in the formation of cyclic products; the vinyl ethers of diethanolamine (I, III), like that of 2-aminoethanol, did not yield substances of the morpholine or oxazolidine type. Indeed, the formation of cyclic products by hydrogen transfer from a hydroxyl group is not very probable owing to steric difficulties.

In the course of the study of the vinylation of di- and tri-ethanolamines we have established also that the presence of the basic nitrogen has a considerably less effect on the vinylation reaction than in the vinylation of 2-aminoethanol and 2-diethylaminoethanol. The vinyl ethers of di- and tri-ethanolamines were formed in good yield (70-85% on the amount of the ethanolamine) in presence of caustic potash, whereas these conditions were quite unsuitable for 2-aminoethanol and 2-diethylaminoethanol, for which it was necessary to replace caustic potash by the potassium derivative of the amino alcohol [1, 2].

The structures of the vinyl ethers obtained were proved by hydrolysis and hydrogenation. The vinyl ethers of di- and tri-ethanolamines were hydrolyzed with dilute sulfuric acid, acetaldehyde and the original ethanolamine being formed. The results of the quantitative estimation of acetaldehyde showed that the mono- and di-vinyl ethers of diethanolamine (I and II) and the trivinyl ether of triethanolamine (III) were readily and completely hydrolyzed by 2% sulfuric acid at room temperature. The mono- and di-vinyl ethers of triethanolamine (IV and V) were only partially hydrolyzed under these conditions, 4-6 hours in a boiling water bath being required for their complete hydrolysis. The hydrogenation of the vinyl ethers of di- and tri-ethanolamines was carried out under pressure in presence of Raney nickel and it resulted in the formation of the corresponding ethyl ethers (Table 4).

The behavior of the vinyl ethers of di- and tri-ethanolamines toward alcohols was studied, and also their polymerization. It was found that the mono- and di-vinyl ethers of diethanolamine (I, II) were inert to the action of alcohols in presence of hydrochloric acid as catalyst (10-12 hours at 150°). Also, the monovinyl ether of diethanolamine (II) did not form an internal cyclic acetal under such conditions.

The vinyl ethers of di- and tri-ethanolamines, like those of 2-amino- and 2-diethylamino-ethanol [1,2], did not polymerize in presence of such catalysts as concentrated hydrochloric acid and ferric chloride under the usual conditions for unsubstituted alkyl vinyl ethers. The ion-catalyzed reactions of vinyl ethers of ethanolamines and, in particular, their polymerization reactions are complicated by the presence of two centers (O and N) in these molecules that can undergo "onium" formation. It is possible that the catalyst forms stable complexes with

the vinyl ether molecule, and these have no catalytic effect for the processes concerned. We have, however, succeeded in bringing about the free-radical polymerization of vinyl ethers of di- and tri-ethanolamines by the use of 2,2'-azobis[2-methylpropionitrile]. The yield and properties of the resulting polymer depended on the structure of the original vinyl ether (Table 5). A peculiar feature of some of the polymers was their three-dimensional structure; their formation could result from the presence of several vinyl or other functional groups in the original monomers.

EXPERIMENTAL

1. Synthesis of Vinyl Ethers of Diethanolamine (I and II)

Diethanolamine, prepared by reaction between ethylene oxide and aqueous ammonia, had the following properties: m.p. 28°; b.p. 155.5–156° and 13 mm; n_D^{30} 1.4755. Its potassium derivative was prepared by reaction with potassium at 30-40°. A mixture of 65.7 g of diethanolamine, 7.3 g of its potassium derivative, and 150 ml of benzene was placed in a 2.5-liter rotating steel autoclave. The autoclave was blown out with acetylene, after which acetylene was passed in up to a pressure of 14-16 atm. The autoclave was heated to 140-150° and maintained at that temperature for 4-6 hours. It was then cooled, a fresh portion of acetylene was passed in, and the autoclave was again heated at the same temperature. The total amount of acetylene passed in was the calculated amount for the vinylation of two hydroxyl groups.

The benzene was distilled off, and the reaction products were separated by vacuum fractionation, which yielded:

Frac. I,	b.p. 85–95°	(9 mm);	71.7 g
Frac. II,	b.p. 98–110°	(9 mm);	14.0 g
Frac. III,	b.p. 115–135°,	(9 mm);	1.0 g
Resin			21.0 g

Redistillation of Fraction I after treatment with sodium yielded 70.0 g (64.2% on the amount of diethanolamine taken) of the divinyl ether of diethanolamine (I), a colorless mobile liquid having an amine odor, soluble in ether, benzene, alcohol, acetone, and dioxane, b.p. 80.5–81.5° and 8 mm; 68–69° and 3.5 mm; n_D^{20} 1.4576; d_4^{20} 0.9491; found MR 45.17; calculated for $C_8H_{15}O_2N$ MR 45.09; found M (cryoscopically in benzene) 148.0; 147.4; calculated M 157.2.

	Found %	C 60.91; 61.06; H 9.60; 9.67; N 8.94; 9.08
$C_8H_{15}O_2N$.	Calculated %	C 61.12; H 9.61; N 8.92

Repeated vacuum fractionation of Fraction II resulted in the isolation of 12.0 g (13.2% on the amount of diethanolamine taken) of the monovinyl ether of diethanolamine (II), a colorless, viscous liquid, readily soluble in ether, benzene and alcohol, poorly soluble in water, b.p. 95° (4 mm); n_D^{20} 1.4687; d_4^{20} 1.007; found MR 36.24; calculated for $C_6H_{13}O_2N$ MR 36.21; found M (cryoscopically in benzene) 134.8; 136.6; calculated M 131.1.

	Found %	C 55.43; 55.24; H 9.97; 9.95; N 10.50; 10.60
$C_6H_{13}O_2N$.	Calculated %	C 54.94; H 9.99; N 10.60

The literature [7] gives b.p. 100-110°/8 mm.

The vinylation of diethanolamine was carried out also in presence of caustic potash and in an aqueous medium. The reaction products were worked up in various ways. The results of the experiments are given in Table 1.

In the vinylation of diethanolamine, and also of triethanolamine, not only the ethanolamine, but also the acetylene, took part in the formation of resin.

2. Synthesis of Vinyl Ethers of Triethanolamine (III, IV, and V)

Triethanolamine was separated from the technical product by distillation and had the following constants: b.p. 178° (3.5 mm); $n_D^{20.5}$ 1.4858; d_4^{20} 1.144. The preparation of vinyl ethers of triethanolamine was carried out as for diethanolamine, with the exception that caustic potash was used as catalyst. The autoclave contained 100 g of triethanolamine, 10 g of caustic potash powder, and 150 ml of benzene, and the reaction temperature was maintained in the range 150-160°. Vinylation was discontinued when about 1.8 mole of acetylene had been adsorbed per mole of triethanolamine.

After removal of solvent, the following fractions were obtained from the reaction products:

Frac. I, b.p. 65 – 70°, – 3.5 mm; n_D^{20} 1.4615; 6.5g
Frac. II, b.p. 70 – 115° – 3.5 mm; n_D^{20} 1.4645; 1.0 g
Frac. III, b.p. 115 – 125° – 3.5 mm; n_D^{20} 1.4692; 4.5g
Frac. IV, b.p. 125 – 130° – 3.5 mm; n_D^{20} 1.4720; 92.5g
Frac. V, b.p. 130 – 140°, – 3.5 mm; n_D^{20} 1.4778; 18.8 g
Frac. VI, b.p. 140 – 145°, – 3.5 mm, n_D^{20} 1.4810; 4.3g
Resin 21.3g

Redistillation of Fractions II and III after treatment with sodium yielded 4.0 g (2.6% on the triethanolamine) of the trivinyl ether of triethanolamine (III): colorless liquid having a feeble odor; soluble in ether and benzene; insoluble in water; b.p. 122° (5 mm); n_D^{20} 1.4678; d_4^{20} 0.9696; found MR 65.04; calculated for $C_{12}H_{21}O_3N$ MR 65.08; found M (cryoscopically in benzene 224.1; 218.9; calculated M 227.3.

Found %: C 63.39; 63.42; H 9.57; 9.54; N 6.48; 6.35
$C_{12}H_{21}O_3N$. Calculated %: C 63.40; H 9.28; N 6.16

TABLE 1

Dependence of the Yield of Vinyl Ethers of Diethanolamine on the Vinylation Conditions

Expt. No.	Solvent	Catalyst (10% on the weight of diethanolamine)	Treatment of reaction product	Yield of crude vinyl ethers (b.p. 72-75° and 94-98° at 5 mm) (% on weight of diethanolamine taken)	Amount of resin (% on weight of diethanolamine)
1	Benzene	Potassium derivative	Distillation	83 – 85	25 – 30
2	Benzene	Potassium derivative	Treatment with water	74 – 75	30 – 32
3	Benzene	Caustic potash	Distillation	70 – 73	40 – 45
4	No solvent	Caustic potash	Distillation	70 – 73	45 – 47
5	Water	Caustic potash	Treatment with water	0.0	116

Repeated fractionation of Fraction IV yielded 90.0 g (66.7% on the triethanolamine) of the divinyl ether of triethanolamine (IV): colorless liquid having a feeble odor; soluble in ether, benzene, and alcohol; insoluble in water; b.p. 125-126° (4.5 mm); n_D^{20} 1.4725; d_4^{20} 1.0022; found MR 56.29; calculated for $C_{10}H_{19}O_3N$ MR 56.20; found M (cryoscopically in benzene) 197.8; 195.1; calculated for $C_{10}H_{19}O_3N$ M 201.3.

Found %: C 59.59; 59.67; H 9.64; 9.60. N 7.05; 7.03
$C_{10}H_{19}O_3N$. Calculated %: C 59.66; H 9.49; N 6.95

The literature [7] gives b.p. 120-130°/8 mm.

Repeated fractionation of Fractions V and VI in a current of nitrogen yielded 4.0 g (3.4% on the triethanolamine) of the monovinyl ether of triethanolamine (V): colorless viscous liquid, which yellowed in the air; soluble in ether, benzene, and alcohol; b.p. 141-142° (3.5 mm); n_D^{20} 1.4805; d_4^{20} 1.0596; found MR 47.01; calculated for $C_8H_{17}O_3N$ MR 47.31; found M (cryoscopically in benzene) 180.1; 180.4; calculated M 175.2.

Found %: C 54.92; 54.84; H 9.69; 9.68; N 8.20; 8.38
$C_8H_{17}O_3N$. Calculated %: C 54.84; H 9.78; N 7.99

Fraction I yielded 6 g of a by-product, b.p. 66-67° (3.5 mm); n_D^{20} 1.4613; d_4^{20} 0.9702; found MR 44.50; found M 155.1; 155.9; calculated M 157.2.

Found %: C 61.33; 61.25; H 9.66; 9.52; N 9.06; 9.05
$C_8H_{15}O_2N$. Calculated %: C 61.12; H 9.62; N 8.91

The investigation of this compound with the object of determining its structure is continuing. The yield of the trivinyl ether of triethanolamine (III) can be raised to 65.0% by the use of 3 moles of acetylene per mole of

triethanolamine. Under these conditions, none of the monovinyl ether could be isolated. When one-third of this amount was absorbed, the yield of the monovinyl ether of triethanolamine (V) attained 9-10%.

The results of experiments on the vinylation of triethanolamine in presence of its potassium derivative and without solvent are given in Table 2.

TABLE 2

Dependence of the Yield of Vinyl Ethers of Triethanolamine on the Vinylation Conditions

Expt. No.	Catalyst (10% on the weight of triethanolamine)	Solvent	Total yield of crude vinyl ethers (b.p. 115-145°/3.5 mm) (% on triethanolamine)	Amount of resin (% on triethanolamine)
1	Potassium derivative	Benzene	80 – 85	10 – 15
2	Caustic potash	Benzene	80 – 85	20 – 25
3	Caustic potash	No solvent	80 – 85	25 – 30

The potassium derivative of triethanolamine, which was used as catalyst, was prepared by heating triethanolamine with potassium at 80-90°. In all of these experiments the amount of acetylene passed in was 3 moles per mole of triethanolamine.

It will be seen from Table 2 that the presence of benzene has no effect on the yield of vinyl ethers of triethanolamine. It is however better to carry out the vinylation in a solvent in order to dilute the acetylene (to avoid an explosion).

3. Hydrolysis of Vinyl Ethers of Di- and Tri-ethanolamines

The vinyl ethers were hydrolyzed with 2% sulfuric acid at room temperature and at higher temperatures. The acetaldehyde liberated was determined quantitatively by the bisulfite method [8]. The results of these determinations are given in Table 3.

TABLE 3

Hydrolysis of Vinyl Ethers of Ethanolamines

Expt. No.	Ether	Degree of hydrolysis of vinyl ether (%)
1	Divinyl Ether of Diethanolamine	95.3
		93.5
2	Monovinyl Ether of Diethanolamine	100.6
		99.6
3	Trivinyl Ether of Triethanolamine	97.8
		98.9
4	Divinyl Ether of Triethanolamine	54.5
		43.0
		100.7*
		99.3*
5	Monovinyl Ether of Triethanolamine	91.4
		91.6
		96.6*
		97.4*

4. Hydrogenation of Vinyl Ethers of Di-and Tri-ethanolamines

A mixture of vinyl ether of the ethanolamine and Raney nickel (5% on the weight of the ether) was placed in a 150-ml rotating autoclave, and the calculated amount of hydrogen was passed in. For the vinylethers of diethanolamine hydrogenation took place at room temperature, but for the vinyl ethers of triethanolamine it was necessary to heat to 150°. The duration of the reaction was 10-12 hours. The reaction product was filtered from the catalyst and distilled. It was purified either by treatment with sodium in the cold followed by distillation, or merely by repeated distillation. The yield of hydrogenation products was 65-70%. The reaction was complicated by the formation of by-products, which were not investigated. The constants of the resulting ethyl ethers are given in Table 4.

5. Polymerization of Vinyl Ethers of Di- and Tri-ethanolamines in presence of 2,2'-Azobis[2-methylpropionitrile]

2,2'-Azobis[2-methylpropionitrile] was purified by recrystallization from methanol, and was obtained as colorless crystals, m.p. 105°. It was added (2% by weight) to the vinyl ether, and the mixture was heated continuously at 60-65° for 100 hours in a sealed glass tube. The treatment given to the reaction products was determined by the properties of the vinyl ethers and of their polymers. The results on the polymerization are given in Table 5.

*Results of hydrolysis at 100° for six hours.

TABLE 4

Ethyl Ethers of Di- and Tri-ethanolamines

No.	Ether	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	MR		Elementary Analysis					
							%C		%H		%N	
					found	calculated	found	calculated	found	calculated	found	calculated
1	Diethyl ether of diethanolamine •	84-86(14)	1.4227	0.8855	46.32	46.03	59.74 59.77	59.60	11.99 11.83	11.88	8.79 8.89	8.69
2	Monoethyl ether of diethanolamine	90-90.5 (4.5)	1.4471	0.9676	37.00	36.68	54.32 54.13	54.14	11.33 11.62	11.35	10.53 10.30	10.52
3	Triethyl ether of triethanolamine••	104(3.5)	1.4388	0.9203	66.65	66.48	61.82 61.75	61.77	11.63 11.64	11.66	6.07 5.92	6.00
4	Diethyl ether of triethanolamine	109-110 (4.5)	1.4418	0.9510	57.14	57.13	58.95 58.85	58.50	11.24 11.41	11.29	7.18 7.15	6.82
5	Monoethyl ether of triethanolamine	136-137 (4.5)	1.4635	1.0259	47.63	47.77	53.98 53.85	54.22	11.06 11.04	10.81	8.12	7.90

TABLE 5

Polymerization of Vinyl Ethers of Di- and Tri-ethanolamines in presence of 2,2'-Azobis[2-methylpropionitrile]

Expt. No.	Ether	Yield of polymer (%)	Nitrogen content of polymer (%)		Molecular weight	Characteristics of polymer
			found	calculated		
1	Divinyl ether of diethanolamine	18.4-21.1	9.02 9.09	8.92	1488 1550	Thick; dark red; soluble in benzene, acetone, and alcohols
2	Monovinyl ether of diethanolamine	5.0-7.0	10.70 10.94	10.67	–	Very thick; yellow; insoluble in the usual solvents
3	Trivinyl ether of triethanolamine	40.0-45.0	6.22 6.31	6.16	–	Hard; yellow; insoluble in the usual solvents; infusible
4	Divinyl ether of triethanolamine	19.6-19.8	7.10 6.91	6.95	–	Ditto
5	Monovinyl ether of triethanolamine	6.0	8.71 8.57	7.99	–	Very thick; yellow; soluble in water and alcohols

In Expt. No. 1 the unchanged vinyl ether was separated from the polymer by vacuum distillation, and the polymer was vacuum-dried (3 mm) at 50-60°. In Expts. No. 2-5 the polymer was precipitated from the reaction product with diethyl

• Data in the literature: • b.p. 198-200° [9]; •• b.p. 134-137° and 12 mm; d_4^{25} 0.936 [10].

ether, washed several times with ether, and dried. Unchanged vinyl ether was separated from the ether solution by distillation. Elementary analysis and molecular weight determinations were carried out on the products isolated, and their solubilities in various solvents were examined.

SUMMARY

1. The vinylation reactions of di- and tri-ethanolamines have been studied.

2. It has been shown that the vinylation of di- and tri-ethanolamines results in the synthesis of full and partial ethers, most of which have been prepared for the first time.

3. It has been shown that the vinyl ethers of diethanolamine, like that of 2-aminoethanol, do not undergo cyclization under the conditions of the synthesis.

4. A study has been made of some reactions of vinyl ethers of di- and tri-ethanolamines which prove their structures.

5. It has been found that the vinyl ethers of di- and tri-ethanolamines are less reactive in ion-catalyzed reactions than unsubstituted alkyl vinyl ethers.

6. It has been shown that the vinyl ethers of di- and tri-ethanolamines can polymerize in presence of 2,2'-azobis[2-methylpropionitrile].

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Received December 23, 1953

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* T.p. = C. B. translation pagination.

BRIEF COMMUNICATIONS

SOLUBILITY OF DOLOMITE IN WATER IN PRESENCE OF CARBONIC ACID

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The contradictory views expressed in the literature concerning the solubility relations of dolomite ($CaCO_3 \cdot MgCO_3$) arise from the absence of experimental data on its solubility. In order to resolve this controversial question, we have made a systematic investigation of the properties of dolomite and have made a very full survey of the dependence of its solubility on conditions, particularly on the partial pressure of carbon dioxide.

The solubility of dolomite and of its mixtures with calcite and magnesite was determined for various temperatures (0°, 55°, 70°) at a given partial pressure of CO_2 (about 1 atm), and for different partial pressures of pCO_2 (about 1 atm, and 0.0012 atm) at a given temperature (25°). The starting materials and the experimental procedure were essentially the same as those previously described [1, 2]. An exception was the Shishim dolomite used; this was purer, no magnesite impurity being present; its composition was 0.27% of insoluble residue, 0.40% of sesquioxides, 53.74% of $CaCO_3$, and 45.46% of $MgCO_3$.

In the work at a low partial pressure of CO_2 (pCO_2), laboratory air was used, this being blown through the reaction vessels with the aid of a water pump. The results of the investigation are given in Fig. 1 in the form of polytherm-polybars of the ternary system $CaCO_3-MgCO_3-H_2O$. All the isotherms of the system consist of three branches, corresponding respectively to the crystallization of calcite, dolomite, and magnesite; but the isotherms vary in character.

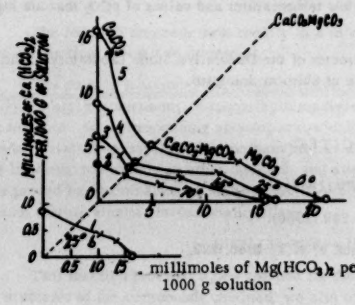

Fig. 1. Polytherm-polybar of the system $CaCO_3-MgCO_3-H_2O$: 1- about 0.0012 atm; 2,3,4,5 - ~1 atm(pCO_2)

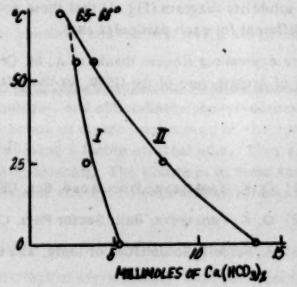

Fig. 2. Solubility polytherms of dolomite and its mixtures with calcite: I- dolomite; II - dolomite + calcite

The broken line joining the point representing the composition of dolomite with the origin (the bisector of the angle made by the axes) intersects the dolomite crystallization isotherms 3, 4, and 5 in points corresponding to the solubility of pure dolomite, thus indicating that dolomite dissolves congruently (without decomposition into its components). The point for cocrystallization of dolomite and calcite (the point a on isotherm 5, Fig. 1) is gradually displaced from the ordinate axis toward the bisector as the temperature rises, and at 70° it has already passed over to the right of the bisector. In other words, at 70° the bisector no longer intersects the dolomite branch of the isotherm; it intersects the calcite branch, which indicates that dolomite now has incongruent solubility (dissolves with decomposition). It will be clear that the temperature at which the point a falls on the bisector must be the temperature of the transition from congruent to incongruent solubility of dolomite.

The polythermal solubility curves for pure dolomite and its mixtures with calcite at a pCO_2 of about 1 atm intersect at a point corresponding to a temperature of 65-66° (Fig. 2), and this will be the transition temperature for

these conditions. As is well known, the solubility of CO_2 in water falls as the temperature rises [3]. As the CO_2 content of the solution falls (in spite of the fact that pCO_2 above the solution remains at about 1 atm), there are corresponding falls in the solubilities of calcite, magnesite, and dolomite (Table and Fig. 1), and there is a simultaneous change in the character of the solubility of dolomite.

TABLE

Solubilities of Dolomite, Calcite, and Magnesite

Temperature (°C)	pCO_2 (atm)	Dolomite	Calcite	Magnesite
		(millimoles of $(HCO_3)_2$ in 1000 g of solution		
0	1	10.74	15.08	22.52
25	1	6.49	9.0	16.50
55	1	6.08	6.09	15.59
70	1	4.58	3.45	–
25	0.0012	1.42	0.81	1.65

When we studied the system at 25° under a pCO_2 of 0.0012 atm, we obtained unequivocal confirmation of the existence of incongruent solubility of dolomite at low concentrations of CO_2 in the solution (isotherm 1, Fig. 1). It will be seen from the diagrams that the crystallization field of dolomite is gradually being narrowed. In the solutions of this system, therefore, dolomite is stable only at certain temperatures and at certain values of pCO_2. It must be pointed out also that the solubilities of the carbonates investigated vary in different ways with changes in the conditions. A comparative examination of the data in the table shows that magnesite is always the most soluble. At a pCO_2 of about 1 atm, dolomite is the least soluble, whereas at a pCO_2 of about 0.0012 atm, calcite is the least soluble, dolomite then taking up second position in the three carbonates. Hence, when the solubility of dolomite is incongruent, its value is higher in comparison with the solubility of calcite than when its solubility is congruent For a value of pCO_2 of about 0.0012 atm and a temperature of 25°, the composition of an equilibrium solution obtained from an initial mixture of dolomite + water always lies at the point on the diagram corresponding to the cocrystallization of dolomite and calcite (the point b on isotherm 1 in Fig. 1), i.e. the values of the solubilities of pure dolomite and of its mixtures with calcite fully coincide at low values of pCO_2, the composition being 0.40 millimole of Ca, 1.02 of Mg, and 1.42 of $(HCO_3)_2$ per 1000 g of solution.

This fact is of significance for the use of carbonate rocks for under-water construction, since dolomites, dolomitic limestones, calcareous dolomites, and other such rocks should have practically the same solubilities at low partial pressures of CO_2, such as are found under natural conditions. The results of the investigation are also of significance for the determination of the conditions under which primary and secondary dolomites have been formed. It follows from the solubility diagram (Fig. 1) that these conditions include low temperatures and values of pCO_2 that are high, though different for each particular case.

We express our sincere thanks to A. M. Orlov, Assistant Director of the Decorative Stone Laboratory of the Academy of Architecture of the USSR, for the gift of a pure sample of Shishim dolomite.

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Received April 7, 1954

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SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

COMMUNICATION 1. SYNTHESIS AND SOME PROPERTIES OF TRIALKYL- AND DIALKYLARYL-(2-CHLOROETHOXY)SILANES

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In previous papers we have laready described the preparation of some new oxygen-containing organosilicon compounds, namely organosilicon acetals prepared by the reaction of trialkyl(and aryl)silanols with vinyl ethers [1, 2, 3]. The trialkyl- and dialkylaryl-(2-haloethoxy)silanes described below, which have the general structure $XCH_2CH_2 \cdot OSiR_3$ (X is halogen; R is alkyl or aryl), form a further example of oxygen-containing organosilicon compounds, and they are of great theoretical interest.

There are several possible methods for the preparation of such compounds. It was found that they were most conveniently prepared by the action of ethylene oxide on alkyl(or alkylaryl)chlorosilanes, and in the present paper we shall describe the syntheses by this method of (2-chloroethoxy)-trimethyl-, -ethyldimethyl-, -diethylmethyl-, -triethyl-, and -diethylphenyl-silanes.

There is little information in the literature on the preparation and properties of compounds of this type. There are only a few results relating to the reactions of ethylene oxide with silicon tetrachloride, chloromethylsilane, and chloroethylsilane [4, 5]. The syntheses of (2-chloroethoxy)-ethyldimethyl-, -diethylmethyl-, and -diethylphenyl-silanes have not been described in the literature. The reaction of trialkyl(or aryl)chlorosilanes with ethylene oxide may be represented as follows:

$$R_3SiCl + CH_2-CH_2 \longrightarrow R_3SiOCH_2CH_2Cl \quad (R = CH_3-,\ C_2H_5-,\ C_6H_5- \text{ etc.})$$

The reaction proceeds most readily in a solvent, e.g. ether or benzene, and the best results are obtained when the mixture is warmed somewhat.

The starting substances for the preparation of trialkyl(or aryl) (2-chloroethoxy)silanes were the corresponding trialkyl(or aryl)chlorosilanes. Chloroethyldimethyl-, chlorodiethylmethyl-, and chlorodiethylphenyl-silanes were prepared from the corresponding alkyl(or aryl)trichlorosilanes by the action of organo-magnesium or -lithium compounds. Trialkyl (or aryl) (2-chloroethoxy)silanes are mobile liquids having a feeble ethereal odor. They are insoluble in water, but soluble in ether, alcohol, and aliphatic and aromatic solvents. The structures of these compounds were proved by examination of their hydrolysis products. The hydrolysis of trialkyl (2-chloroethoxy)silanes with aqueous caustic alkalis yielded trialkylsilanols:

$$ClCH_2CH_2OSiR_3 + HOH \longrightarrow R_3SiOH + HO \cdot CH_2CH_2Cl.$$

This reaction provides a new method for the preparation of trialkyl(or aryl)silanols. With the object of proving the structures of the compounds obtained, we also carried out the reaction of chlorodiethylphenylsilane with 2-chloroethanol. A substance was isolated which corresponded in its properties to (2-chloroethoxy)diethylphenylsilane, which we had prepared from ethylene oxide and chlorodiethylphenylsilane.

In the experimental part we have described the reaction of ethylene oxide with chlorotriethylsilane. The syntheses of (2-chloroethoxy)-trimethyl-, -ethyldimethyl-, and -diethylmethyl-silanes were similar to that of (2-chloroethoxy)triethylsilane. In the preparation of (2-chloroethoxy)diethylphenylsilane, the most satisfactory results were obtained when the reaction was carried out in benzene at 70-80°. Some of the physicochemical properties of the compounds obtained are given in the table.

EXPERIMENTAL

1. Preparation of (2-Chloroethyoxy)triethylsilane

A mixture of 14.6 g (0.1 mole) of chlorotriethylsilane and 200 ml of dry ether was prepared in a three-necked round-bottomed flask provided with mechanical stirrer, thermometer, tube for passage of gas, and reflux condenser. The reaction flask was placed in a water bath, and dried ethylene oxide was passed through the reaction mixture at

TABLE 1

Physicochemical Properties of some Trialkyl- and Dialkylaryl—(2-chloroethoxy)silanes

Name of substance	Formula	Original organosilicon compound			
		Formula	n_D^{20}	d_4^{20}	b.p. in °C (p in mm Hg)
(2-Chloroethoxy)trimethylsilane	$(CH_3)_3SiOCH_2CH_2Cl$	$(CH_3)SiCl$	1.3804	0.8580	58.0(757)mm
(2-Chloroethoxy)ethyldimethylsilane			1.4105	0.8657	89.0
(2-Chloroethoxy)diethylmethylsilane			1.4259	0.8936	119.0
(2-Chloroethoxy)triethylsilane	$(C_2H_5)_3SiOCH_2CH_2Cl$	$(C_2H_5)_3SiCl$	1.4320	0.8977	143-145 (757)
(2-Chloroethoxy)diethylphenylsilane			1.5130	1.0252	227-230(757)

30°. The ethereal solution was distilled, and a further distillation of the reaction product then yielded 16.00 g (82.0%) of (2-chloroethoxy)triethylsilane, b.p. 70.0-70.3 (5.5 mm); n_D^{20} 1.4406; d_4^{20} 0.9499. Found MR_D 54.40; calculated for $C_8H_{19}SiOCl$ MR_D 54.12.

Found %: C 49.48; 49.51; H 9.75; 9.62; Cl 18.00; 18.10

$C_8H_{19}SiOCl$. Calculated %: C 49.33; H 9.83; Cl 18.28

2. Hydrolysis of (2-Chloroethoxy)triethylsilane

The hydrolysis was carried out in a three-necked flask provided with stirrer, dropping funnel, and thermometer. A mixture of 19.5 g (0.1 mole) of (2-chloroethoxy)triethylsilane, 100 ml of ether, and 1-2 drops of phenolphthalein indicator was prepared in the flask, and this was then stirred while 200-210 ml of 2% NaOH was added slowly over a period of one hour. Stirring was continued for 3-4 hours. Fractionation of the ether layer yielded 9.5 g (72.8%) of triethylsilanol, b.p. 154° (757 mm); n_D^{20} 1.4340; d_4^{20} 0.8645.

SUMMARY

1. The reaction of ethylene oxide with the following trialkyl(or aryl)chlorosilanes has been investigated: chlorotrimethyl-, chloroethyldimethyl-, chlorodiethylmethyl-, chlorotriethyl-, and chlorodiethylphenyl-silanes.

2. The following compounds have been prepared for the first time and characterized: (2-chloroethoxy)-triethyl-, and (2-chloroethoxy)diethylphenyl-silanes.

3. The proposed method is probably general for the preparation of various trialkyl(or aryl) (2-haloethoxy) silanes from ethylene oxide and trialkyl(or aryl)chlorosilanes.

Received May 19, 1954

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Yield of 2-chloroethoxy derivative (%)	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	MR_D		Analysis (%)					
						C		H		Cl	
				Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
86.44	130-131 (758)	1.4142	0.9460	40.51	40.35	39.29	39.31 39.20	8.58	8.88 8.60	23.24	23.00 23.15
84.6	71-72 (39)	1.4262	0.9467	45.14	44.97	45.14	45.29 45.20	9.07	9.10 9.00	21.26	21.00 21.20
90.2	67-68 (13)	1.4316	0.9478	49.77	49.41	46.52	46.67 46.70	9.48	9.32 9.54	19.62	19.12 19.41
82.0	70.0-70.3	1.4406	0.9499	54.45	54.12	49.33	49.48 49.51	9.83	9.75 9.62	18.28	18.00 18.10
80.1	128-130 (7.0) (5.5)	1.5062	1.0562	69.59	69.09	59.35	59.09 59.00	7.82	7.66 7.45	14.60	14.35 14.30

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SYNTHESIS OF DIALLYLSILANES

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Only four diallylsilanes ($CH_2 = CHCH_2)_2SiR_2$ are known: $(C_3H_5)_2Si(C_3H_5)_2$ [1], $CH_3HSi(C_3H_5)_2$ [2], $(CH_3)_2Si(C_3H_5)_2$ [2], and $H_2Si(C_3H_5)_2$ [3]. Diallysilanes, however, are beginning to be used in copolymerization reactions, which may be carried out under atmospheric pressure [4], or under high pressures. With the object of extending our knowledge of the properties of diallylsilanes, in the present investigation we have synthesized four new diallysilanes, including three containing aryl radicals (see table). The properties of the previously unknown dichloromethyl-1-naphthylsilane are also given in the table. Apart from the synthesis of the new diallysilanes, we had occasion to repeat the syntheses of some mono-, di-, and tri-allylsilanes, and for this purpose we used allyl chloride, bromide, and iodide. As stated in a previous communication [2], the replacement of allyl chloride by the bromide greatly reduces (by a factor of 5-8) the amount of ether needed. Allyl iodide [5] requires the same reaction conditions as the bromide (except that it is necessary to distil over sodium to remove the iodine liberated), and it gives higher yields of $(CH_3)_2SiC_3H_5$, $(CH_3)_2Si(C_3H_5)_2$, and $(C_2H_5)_3SiC_3H_5$ than allyl bromide. It was found, however, that allyl iodide cannot be used at all for the synthesis of $(C_6H_5)_2Si(C_3H_5)_2$, $(1\text{-}C_{10}H_7)CH_3Si(C_3H_5)_2$, and $C_6H_5CH_3Si(C_3H_5)_2$, and low yields are obtained of $CH_3Si(C_3H_5)_3$ and $C_2H_5HSi(C_3H_5)_2$, since these substances undergo much polymerization during rectification.

TABLE

Diallylsilanes and Alkylaryldichlorosilanes

No.	Diallylsilane	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	MRf** found	MRf** calculated	Yield (%)
1	$(C_3H_5)HSi(C_3H_5)_2$*	147.5 (740)	1.4510	0.7808	48.37	48.36	29
2	$(CH_3)_2Si(C_3H_5)_2$	135.5 (760)	1.4420	0.7679	48.20	48.22	77.5
3	$(C_6H_5)_2Si(C_3H_5)_2$*	140.5 (2)	1.5750	0.9955	87.77	87.86	62
4	$(C_6H_5)CH_3Si(C_3H_5)_2$*	242 (770)	1.5220	0.9095	67.85	68.04	73.2
5	$(1\text{-}C_{10}H_7)CH_3Si(C_3H_5)_2$*	140 (1)	1.5879	0.9908	85.72	83.34	53.2
6	$C_6H_5(CH_3)SiCl_2$	206-7(757)	1.5180	1.1866	48.80	49.32	56
7	$1\text{-}C_{10}H_7(CH_3)SiCl_2$*	122 (1)	1.6025	1.2333	66.98	64.66	33.2

Diallylethylsilane $C_2H_5HSi(C_3H_5)_2$ (1). A mixture of 25.3 g of $C_2H_5HSiCl_2$ and 100 g of C_3H_5I was added over a period of four hours to 20 g of Mg contained in 250 ml of ether. The ether was distilled off, and the residue was heated for two hours in a boiling water bath. The yield of (1) was 8 g, the remainder being high-boiling polymer.

	Found %:	C 68.26; 68.40; H 11.24; 11.46
$C_8H_{16}Si$.	Calculated %:	C 68.5; H 11.5

Diallyldimethylsilane $(CH_3)_2Si(C_3H_5)_2$ (2). A mixture of 129 g of $(CH_3)_2SiCl_2$ and 504 of C_3H_5I was added over a period of ten hours to 110 g of Mg in 1 liter of ether. The ether was removed, and the residue heated for ten hours at about 100°. The yield of (2) was 112 g.

Diallyldiphenylsilane $(C_6H_5)_2Si(C_3H_5)_2$ (3). A mixture of 38 g of $(C_6H_5)_2SiCl_2$ and 35 g of C_3H_5Cl was added over a period of 2 hours 30 minutes to 22 g of Mg in 800 ml of ether. The residue after removal of ether was heated for about eight hours in a boiling water bath. The yield of (3) was 28 g.

	Found %:	C 82.15; 82.30; H 7.74; 7.77; Si 10.26; 10.57
$C_{18}H_{20}Si$.	Calculated %:	C 81.76; H 7.62; Si 10.61

Diallylmethylphenylsilane $CH_3C_6H_5Si(C_3H_5)_2$ (4). A mixture of 120 g of $(CH_3)C_6H_5SiCl_2$ and 135 g of C_3H_5Cl was added over a period of four hours to 66 g of Mg in 3 liters of ether. The ether was driven off, and the residue

* Prepared for the first time.

** In the calculation, the corrections that we have introduced for the allyl group [6] and the ethyl group [3] are taken into account.

was heated for ten hours at about 100°. The yield of (4) was 93 g.

	Found %:	C 77.27; 77.11;	H 8.82; 8.94;	Si 13.90; 14.08	
$C_{13}H_{18}Si$.	Calculated %:	C 77.17;	H 8.97;	Si 13.87	

Diallylmethyl-1-naphthylsilane $1\text{-}C_{10}H_7CH_3Si(C_3H_5)_2$ (5). A mixture of 75 g of $1\text{-}C_{10}H_7CH_3SiCl_2$ and 98 g of C_3H_5Cl was added over a period of 90 minutes to 47 g of Mg in 1800 ml of ether. After removal of ether, the residue was heated for twelve hours. The yield of (5) was 39 g.

	Found %:	C 80.83; 80.84;	H 8.02; 8.11;	Si 11.25; 11.04	$C_{17}H_{20}Si$.
$C_{17}H_{20}Si$.	Calculated %:	C 80.90;	H 7.99;	Si 11.12	

Dichloromethyl-1-naphthylsilane $1\text{-}C_{10}H_7CH_3SiCl_2$ (7). 1-Naphthyllithium, prepared in 1 liter of ether from 28.9 g of Li and 414 g of $1\text{-}C_{10}H_7Br$ was added to an ice-cooled solution of 480 g of CH_3SiCl_3 in 500 ml of ether; the addition was spread over 35 minutes. After four hours the precipitate was filtered off. Two distillations yielded 160 g of (7).

	Found %:	C 55.01; 54.96;	H 4.21; 4.22;	Cl 29.10; 29.70;	Si 11.93; 11.78	
$C_{11}H_{10}SiCl_2$.	Calculated %:	C 54.78;	H 4.48;	Cl 29.40;	Si 11.64	

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Received July 12, 1954

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